

Thermal stability of low temperature ionic liquids revisited

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Abstract

The range of thermal stability of low temperature ionic liquids published in the literature (often $>400\text{ }^{\circ}\text{C}$) is severely overrated. The decomposition temperature calculated from fast TGA scans in a protective atmosphere does not imply a long-term thermal stability below that temperature. Even at temperatures as low as $200\text{ }^{\circ}\text{C}$, 1-alkyl-3-methylimidazolium phosphates (alkyl = C4–C10) and 1-decyl-3-methylimidazolium triflate showed a slow, but appreciable mass loss. On the other hand, 1-butyl-3-methylimidazolium triflate was stable at $200\text{ }^{\circ}\text{C}$. The carbonization occurred in most studies salts irrespectively of the nature of the anion (hexafluorophosphate, triflate), but the salts with a shorter side chain (C4) did not show changes in their color after conditioning for 10 h at $200\text{ }^{\circ}\text{C}$ in air. 1-Butyl-3-methylimidazolium triflate shows extremely good wettability against aluminum oxide and silver at elevated temperatures. Addition of silica (amorphous or quartz) accelerates the thermal decomposition of 1-alkyl-3-methylimidazolium phosphates and triflates at $200\text{ }^{\circ}\text{C}$, while the effect of other ceramic powders (titania, alumina) is less significant.

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1. Introduction

The thermal stability of 1-alkyl-3-methylimidazolium salts (low temperature ionic liquids) has been extensively studied [1–6], but vast majority of the reported data are the temperatures of the onset of degradation (up to $481\text{ }^{\circ}\text{C}$) based on fast (10 or $20\text{ }^{\circ}\text{C}/\text{min}$) TGA scans, collected under dry nitrogen. The TGA onset point has an advantage of being easily measured and reproducible value, dependent on a number of controllable parameters: scan rate, gas flow rate, and mass of the sample, but it has a limited significance in respect to a long-term thermal stability of the low temperature ionic liquids. Our concerns about the technological significance of the fast TGA scans in low temperature ionic liquids under protective gas atmosphere are as follows:

- The decomposition reaction is too slow to allow equilibration at certain temperature.
- The heat transfer in the ionic liquid is slow thus, the temperature in the ionic liquid may lag behind.

- The decomposition of ionic liquids with inorganic cations is endothermic [4]. The reaction heat is taken from the neighboring ionic liquid and this enhances the lag.
- Some potential technological applications of the ionic liquids may exclude a protective atmosphere at all, or at least the requirement of protective atmosphere substantially increases the cost.
- The results obtained in the presence of different chemical compounds added to ionic liquids (deliberate modification of properties) or present as impurities (e.g., ambient moisture), are more relevant to practical applications than the results obtained with very pure ionic liquids. The effect of typical impurities (water, chlorides) in ionic liquids on their thermal decomposition is rather insignificant [5,6], but a little is known about the effects of other additives. It should be emphasized that low temperature ionic liquids are difficult to purify, and the level of impurities is probably the least controlled parameter in the studies of their thermal stability.

The temperature ranges of thermal stability (based on fast scans in nitrogen) were cited in many papers (including reviews), often without sufficient experimental details, and a technology-oriented reader looking for long-term stability

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data may be misled. As an example of such misleading statements we cite the following phrase from a recent article [7]: “ILs form glasses at low temperatures and have minimal vapor pressures up to their thermal decomposition temperature, which was determined for [emim][PF₆] as 648.15 K [4].”

So far, long-term thermal stability of the low temperature ionic liquids, has been studied only under protective atmosphere [6]. In the present study we report on long-term thermal stability of the low temperature ionic liquids in the presence of air. The fast scans did not indicate any substantial difference in onset of degradation between nitrogen and oxygen atmosphere in some salts [4], and the presence of oxygen accelerated the thermal decomposition of a few other salts [8], but these results are not necessarily relevant to long-term stability. A few results were obtained under protective atmosphere, and also a few fast TGA scans are presented for comparison. The effect of ceramic powders having a high specific surface area on the thermal decomposition process was also studied.

2. Experimental

The 1-alkyl-3-methylimidazolium chlorides (alkyl = butyl, hexyl, octyl, or decyl) were synthesized from reagent grade 1-methylimidazole and n-alkyl chlorides from Fluka and Sigma–Aldrich. The ionic liquids were produced by metathesis method from 1,3-dialkylimidazolium chlorides and ammonium or silver salts of hexafluorophosphoric or triflic acid in acetonitrile. After final drying, the ionic liquids were stored in air-tight plastic bottles, but no other precautions were undertaken against absorption of atmospheric moisture. These ionic liquids are referred to as “wet”. Small portions of each ionic liquid was kept in a desiccator containing a drying agent and the bottles were opened only in a dry box. These ionic liquids are referred to as “dry”. The level of the main impurities in the ionic liquids is summarized in Table 1. The concentration of chlorides was determined using Vollhard method. The concentration of water in “dry” ionic liquids was determined from the area of the peak at about 3.2 ppm (related to TMS) in the NMR spectra of the ionic liquids in DMSO-6D [9]. The ionic liquids contain also an unknown impurity that produces a peak at about 2.7 ppm. About 1% of the hydrogen

in the system was a component of this impurity. The same impurity was found in acetonitrile, that was used as a solvent in the synthesis of the ionic liquids. The other peaks in the NMR spectra were identified as the peaks of the major component, the proportions of their areas roughly matched the theoretical formula. Considering the results reported in Table 1 we suppose that the purity of our ionic liquids was not worse than in other thermochemical studies. Nevertheless, the effect of the impurities on the course of the TGA curves cannot be excluded.

Netzsch TG 209 was used to collect TGA scans. Netzsch offers two types of crucibles (from aluminum and from aluminum oxide), and a few experiments were carried out in home made silver crucibles. The mass of the ionic liquid in one scan was usually 4–15 mg. It was difficult to produce small drops of exactly the same mass due to a high viscosity of the ionic liquids.

Different temperature programs used in this study are described in Section 3. Before each TGA measurement the oven was kept at 700 °C for at least 1 h to burn down the leftovers from previous runs.

Reagent grade amorphous silica, α -alumina and anatase (TiO₂), average grain size 0.007, 3, and 0.3 μ m, respectively, and technical quartz, average grain size 2 μ m (cf. [10] for detailed characterization), were used to study the effect of ceramic powders on the thermal stability. The mass fraction of the ceramic powder in the ionic liquid was about 1/3.

3. Results and discussion

3.1. Fast scans

Fig. 1 shows the effect of the mass of the ionic liquid on the results of fast scans at otherwise identical conditions (in aluminum oxide crucibles). The increase in the mass of the sample by a factor of 2 induced an increase in the apparent decomposition temperature (determined from the step tangent [4]) by about 50 °C. Thus, the decomposition temperatures determined from the fast scans reported in the literature [1–6] have a relative character and they are valid only for certain mass of the ionic liquid (which is usually not reported). Considering differences in the mass of ionic liquids used in the experiments, the discrepancies in the decomposition temperatures reported in different studies in the range of 50 K are not surprising, and compilations of decomposition temperatures taken from different sources may lead to erroneous conclusions as to relative thermal stabilities of different ionic liquids. Certainly, the mass effect on the fast TGA scans depends on the type of instrument, e.g., the position of the thermocouple relative to the sample.

Also apparent anomalies, e.g., the increase in thermal stability of certain ionic liquid in the presence of admixtures of water, while in most ionic liquids the thermal stability

Table 1
Impurities in the dry ionic liquids/mass%

| Ionic liquid | Mass (%) | |
|---------------------|------------------|------|
| | H ₂ O | Cl |
| BMI triflate | 0.07 | 0.16 |
| DMI triflate | 0.08 | 0.15 |
| BMI PF ₆ | 0.02 | 0.61 |
| HMI PF ₆ | 0.06 | 0.08 |
| MOI PF ₆ | 0 | 0.34 |

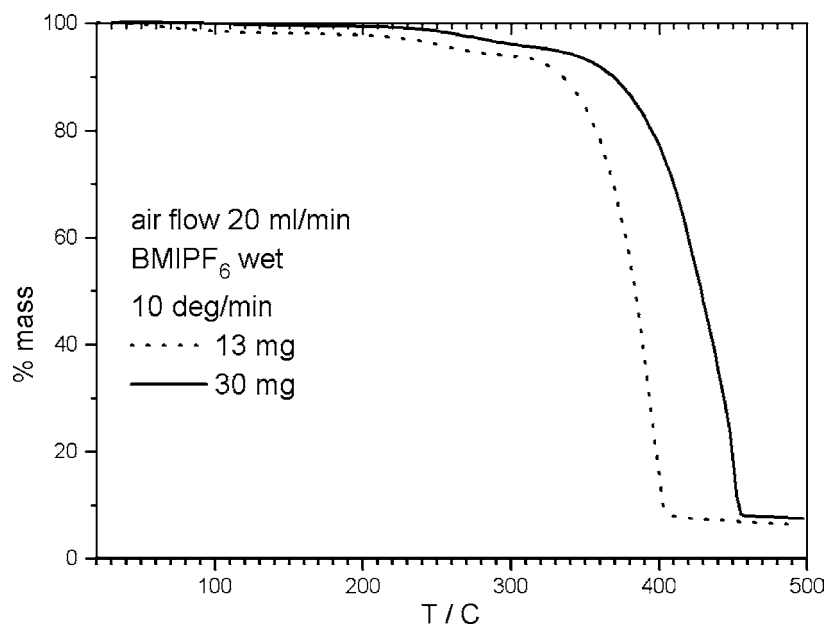


Fig. 1. The effect of the mass of the specimen on the course of fast TGA scans.

was somewhat depressed by the moisture [5], can be very well due to a similar effect as that presented in Fig. 1. In other words, studies of the influence of various factors on the course of fast scans, produce meaningful results only when the masses of the ionic liquids in all compared experiments are nearly equal.

Fig. 2 compares scans taken at two different rates (in aluminum oxide crucibles). The decrease in the scan rate by a factor of 10 produced a dramatic shift in the apparent decomposition temperature. Figs. 1 and 2 show typical trends, which have been also observed with other ionic liquids.

Aluminum crucibles react with hexafluorophosphates [4] at high temperatures, and this substantially affects the course of thermogravimetric curves. Our experiments confirmed that apparent decomposition temperatures in aluminum crucibles were substantially lower than in aluminum oxide crucibles for hexafluorophosphates, and slightly lower for triflates. On the other hand, the difference between the results obtained with aluminum oxide crucibles (commercially available) and silver crucibles (home made) was rather insignificant. Therefore, the difference between aluminum and aluminum oxide crucibles is rather due to reactivity of

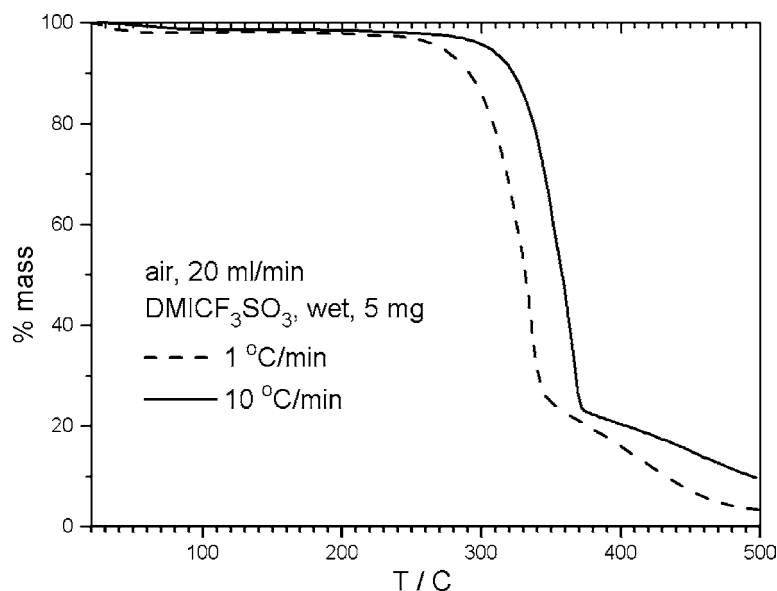


Fig. 2. The effect of the scan rate on the course of fast TGA scans.

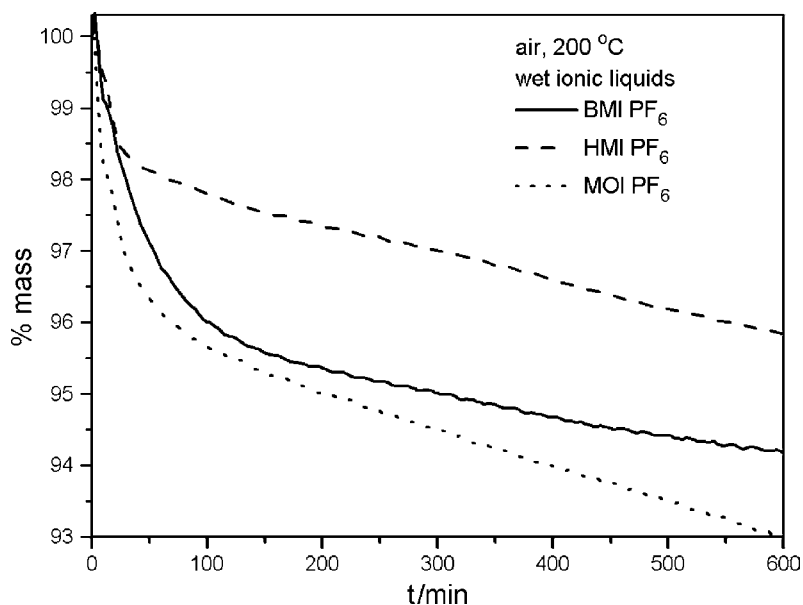


Fig. 3. Thermal stability of hexafluorophosphates at 200 °C in air.

aluminum than to the difference in heat conductance between the crucible materials. All fast scans (maximum temperature 500 °C) resulted in production of charcoal in the crucible. The amount of charcoal left over depends on the nature of the ionic liquid and on the mass of sample.

The present results confirmed that the course of fast TGA scans depends on the anion (triflates show substantially higher thermal stability than hexafluorophosphates) while the effect of the cation (1-alkyl-3-methylimidazolium; alkyl = butyl, hexyl, octyl, or decyl) is rather insignificant.

3.2. Long-term stability

Typical kinetic curves of thermal decomposition at constant temperature in the presence of air are illustrated in Fig. 3. The initial steep portion is followed by a linear step with a nearly constant slope. There is no generally accepted quantitative definition of the long-term stability. We believe that the slope of the linear portion rather than the overall mass loss after certain time elapsed should be used to characterize the long-term stability of the main component of the ionic liquid. Namely, typical impurities, e.g., halides [11] de-

compose at lower temperatures than hexafluorophosphates of triflates. Thus, the initial steep portion is rather the indicator of the purity of the ionic liquid than of its long term thermal stability.

The numerical values calculated from these curves (Table 2) and discussed below refer to certain mass of the ionic liquid (about 11 mg in this case). Even in “dry” ionic liquids there was a substantial (0.2–1.5%) steep portion in the thermogravimetric curves. The slopes of the linear step are reported in Table 2. The slopes obtained in nitrogen were substantially lower than in air at otherwise the same conditions for hexafluorophosphates. On the other hand, the difference in slope between air and nitrogen for 1-decyl-3-methylimidazolium triflate was rather insignificant.

After conditioning for 10 h at selected temperature, the sample was cooled down, and its appearance was examined. The changes in color are reported in Table 2. Certain ionic liquids produced wet spots under the crucibles in the TGA device after long-term experiments. In order to explain the origin of these spots the following experiments were carried out. The crucible with the ionic liquid was heated at 200 °C for a few hours, then the temperature was raised to 400 °C

Table 2
Behavior of low temperature ionic liquids (wet) at 200 °C

| Ionic liquid (wet) | Mass loss (%/h) | | Color after 10 h @200 °C | | Wet spots (see text) after 10 h @200 °C | |
|---------------------|-----------------|----------------|--------------------------|----------------|---|----------------|
| | Air | N ₂ | Air | N ₂ | Air | N ₂ |
| BMI triflate | 0 | 0 | No change | | Yes | |
| DMI triflate | 0.03 | 0.04 | Black | No change | Yes | No |
| BMI PF ₆ | 0.17 | 0.11 | No change | No change | Yes | No |
| HMI PF ₆ | 0.21 | 0.07 | Brown | Brownish | No | No |
| MOI PF ₆ | 0.32 | 0.06 | Brown | No change | No | No |

for a few minutes, and the sample was cooled down. This resulted in black color on internal and external walls of the crucible (the range of coloration dependent of the time of conditioning at 200 °C), which marked the range covered by a film of the ionic liquid. These experiments indicate that certain ionic liquids creep up the walls of the crucible (rather than infiltrate the bottom of the crucible). The wet spots were observed chiefly for 1-butyl-3-methylimidazolium salts, also with silver crucibles. High wettability at elevated temperature (first reported in the present study) may be relevant to possible technical applications of ionic liquids involving temperatures of about 200 °C. The difference in the wetting behavior between 1-butyl-3-methylimidazolium salts and their long chain analogs is in line with the strong effect of the chain length on the viscosity at room temperature [12]. Apparently, the chain–chain interactions play a dominating role in the rheological and surface properties of the ionic liquids at room and elevated temperatures.

Out of five ionic liquids studied (Table 2) only 1-butyl-3-methylimidazolium triflate shows a long-term stability in air at 200 °C. Although the mass loss in 1-decyl-3-methylimidazolium triflate was difficult to quantize, the change in its color indicated some level of degradation. In the series of 1-alkyl-3-methylimidazolium hexafluorophosphates, the increase in the chain length induces a systematic decrease in the thermal stability in air. Very likely this trend is common for various anions. Thus, the short chain 1-alkyl-3-methylimidazolium salts are more promising for any application that requires a long-term thermal stability in air than their long chain analogs. An opposite trend observed in nitrogen, i.e., increase in the long-term stability when the chain length increases (Table 2) is probably due to increasing viscosity.

At temperatures above 200 °C, even 1-butyl-3-methylimidazolium triflate becomes unstable in air, and the mass loss kinetics is similar to that shown in Fig. 3. Moreover, 1-butyl-3-methylimidazolium triflate changes its color (becomes slightly darker) after 10 h at temperature as low as 230 °C. Interestingly, there was no substantial change in color of 1-butyl-3-methylimidazolium triflate after conditioning for 6 h at 250 °C in nitrogen atmosphere, but the rate of mass loss in air and in nitrogen was practically the same (0.56%/h) at 250 °C. The significance of the above rate of mass loss is limited, namely wet spots under the crucible were found after all long-term TGA experiments with 1-butyl-3-methylimidazolium triflate in air at 200–250 °C. The discussed above creeping of the ionic liquid may then contribute to the mass loss. So far no satisfactory solution of this problem has been found.

Instability of the low temperature ionic liquids (except for 1-butyl-3-methylimidazolium triflate) in air at 200 °C is not surprising. Decomposition rates on the order of 1%/h in nitrogen atmosphere at 250 °C were reported [6] for EMIBF₄ and BMIBF₄.

The effect of ceramic powders on the thermal stability of dry 1-hexyl-3-methylimidazolium and 1-methyl-3-octylimidazolium phosphate in air at 200 °C is illustrated in Figs. 4 and 5. Similar effects were observed with other ionic liquids. These results have rather qualitative character since no effort was made to homogenize the mixture, also the mass of the ionic liquid and of the ceramic powder varies from one experiment to another.

The presence of silica dramatically accelerates the thermal decomposition. Separate experiments (results not shown here) indicated that silica itself was thermally stable at 200 °C, thus the mass loss in Figs. 4 and 5 was entirely

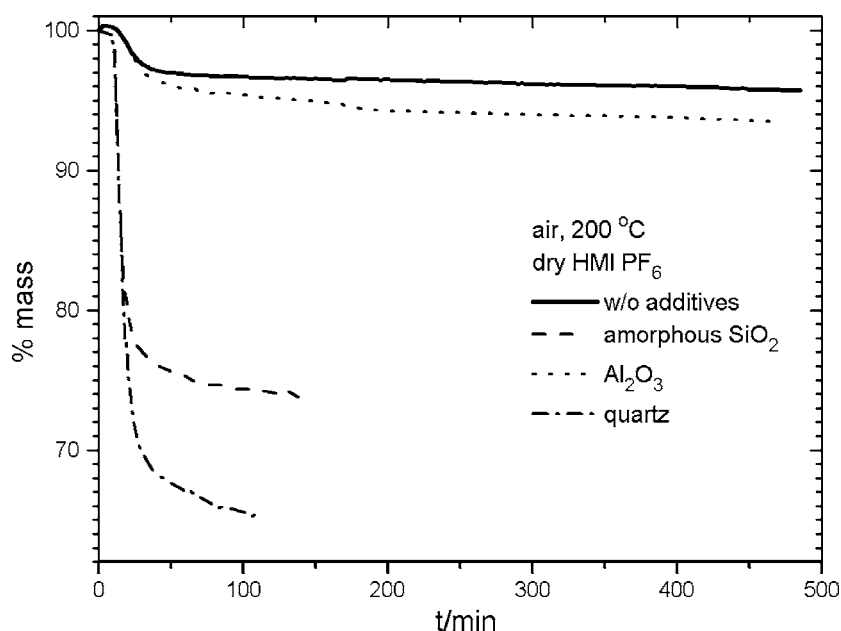


Fig. 4. The effect of ceramic powders on the thermal stability of 1-hexyl-3-methylimidazolium phosphate in air at 200 °C.

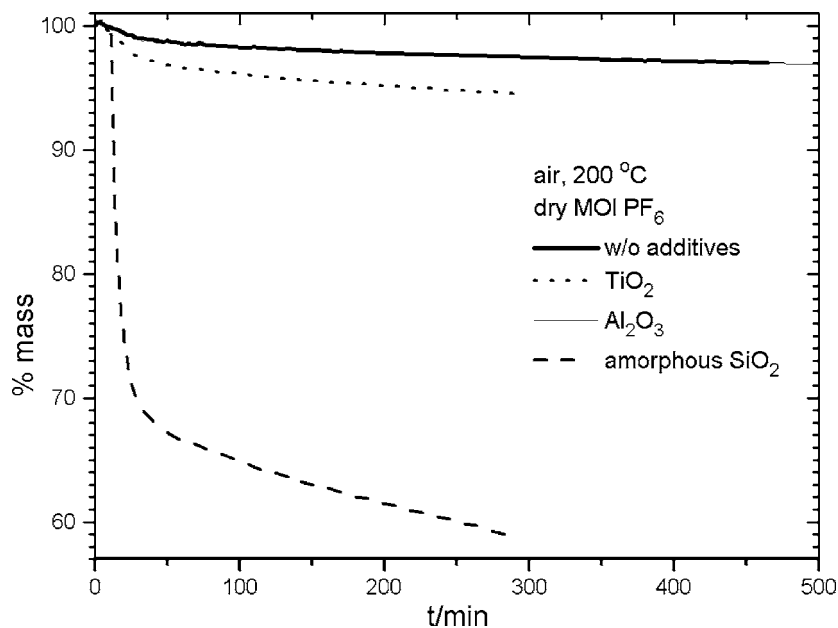


Fig. 5. The effect of ceramic powders on the thermal stability of 1-methyl-3-octylimidazolium phosphate in air at 200 °C.

due to thermal decomposition of the ionic liquids. The effect of titania on the rate of the thermal decomposition was less significant, and the curve obtained with alumina was practically identical as in absence of ceramic powders for 1-methyl-3-octylimidazolium phosphate. Thus, presence of silica, especially in a form of fine powders must be avoided in applications where long-term thermal stability of ionic liquids is required. Interestingly, the effect of ceramic powders on the thermal stability of ionic liquids at 200 °C is correlated with their points of zero charge PZC. Silica has a PZC at very low pH, titania has a PZC at pH 6, and alumina has a PZC at pH 9 [13]. Apparently, the acidity of the surface is a factor that accelerates the thermal decomposition. Silica induced thermal decomposition of 1-butyl-3-methylimidazolium triflate (which was stable at 200 °C in the absence of silica), although the effect was less significant than that shown in Figs. 4 and 5. The presence of catalyst (silica) affects chiefly the initial steep portion of the kinetic curves of thermal decomposition. This result is also very important, namely the mass loss over the first few minutes is not necessarily a good method to estimate the amount of the concentration of volatile impurities in the ionic liquids.

Evacuation at elevated temperatures is usually the final step in the synthesis of the ionic liquids. Working at higher temperatures saves time, but there is also a risk that the ionic liquid decomposes. The present study indicates the temperature/time limits for such an evacuation.

The decomposition rates of “dry” hexafluorophosphates in air (defined as the slope of the linear segment, cf. Fig. 3) were lower than those of “wet” hexafluorophosphates at otherwise the same conditions. On the other hand, the difference in slope between “dry” and “wet”

1-decyl-3-methylimidazolium triflate (in air) was rather insignificant.

4. Conclusion

1-Alkyl-3-methylimidazolium phosphates are not suitable for applications that require long-term stability at 200 °C or more. At 200 °C the rate of thermal decomposition is on the order of a few per mille per hour, and it is higher in air than in nitrogen, especially for the long-chain (C₈–C₁₀) derivatives. In air the long-chain derivatives undergo carbonization that is manifested by dark color. 1-butyl-3-methylimidazolium triflate can be used at temperatures slightly above 200 °C in the absence of silica. Silica (quartz or amorphous) accelerates the thermal decomposition of all ionic liquids studied. The mechanism of this phenomenon is unknown. Probably it is related to the competition between two acids (silica on the one hand and triflic or hexafluorophosphoric acid on the other) for the amine.

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