

Quantum chemical aided prediction of the thermal decomposition mechanisms and temperatures of ionic liquids

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Abstract

The long-term thermal stability of ionic liquids is of utmost importance for their industrial application. Although the thermal decomposition temperatures of various ionic liquids have been measured previously, experimental data on the thermal decomposition mechanisms and kinetics are scarce. It is desirable to develop quantitative chemical tools that can predict thermal decomposition mechanisms and temperatures (kinetics) of ionic liquids. In this work ab initio quantum chemical calculations (DFT-B3LYP) have been used to predict thermal decomposition mechanisms, temperatures and the activation energies of the thermal breakdown reactions. These quantum chemical calculations proved to be an excellent method to predict the thermal stability of various ionic liquids.

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1. Introduction

Ionic liquids (ILs) have been described as potential environmentally benign replacements for volatile organic solvents in a variety of applications [1,2]. ILs are organic salts that have melting points close to room temperature. Their most remarkable property is that the vapor pressure of ILs at room temperature is negligibly small. Therefore, ILs are non-volatile and non-flammable. Moreover, ILs have a wide liquid temperature range and a relatively high thermal and electrochemical stability. In principle, it is possible to tune the physical and chemical properties of ILs by varying the nature of the anions and cations. In this way ILs can be made task-specific for a certain application. Applications include the usage of ILs as electrolytes in electrochemical devices [3–6], the usage as solvents in chemical synthesis and catalysis [1,2,7–9] and separation technology

[10,11] and the usage as lubricants or as heat-transfer fluids [12]. Because these applications often require prolonged operation at elevated temperatures, it is essential to know the long-term stability of ILs.

The thermal stability of an IL is manifested by the height of the thermal decomposition temperature and has been extensively studied for a variety of ILs using thermogravimetric analysis (TGA) at a single linear heating rate (10–20 °C/min) [13–25]. It was found that the decomposition temperature strongly depends on the IL structure. ILs with poorly proton-abstracting anions, such as the bis(trifluoromethylsulfonyl)imide anion, are most stable to high-temperature decomposition ($T_{\text{decomp}} \approx 420$ °C), whereas ILs with nucleophilic and highly proton-abstracting anions, such as halides, decompose at much lower temperatures ($T_{\text{decomp}} \approx 270$ °C) [13–20]. The decomposition temperature of ILs also depends on the type of cation. For example, the imidazolium-based ILs appear to have a better thermal stability than the pyridinium-based and tetraalkylammonium-based ILs [13,21–23]. Methyl substitution on the 2-position of the imidazolium-cation enhances the thermal stability due to the removal of the acidic hydrogen [14,19,23,24]. The alkyl chain

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length of the alkyl group on the cation does not have a large effect on the thermal stability of the ILs [25]. Finally, it was found that the conditions of measurement (atmosphere, pan composition) have some impact on the thermal stability of the IL [13]. For example, imidazolium-based hexafluorophosphate ILs decompose at lower temperatures in the presence of an air atmosphere and an aluminum pan, compared to a nitrogen atmosphere and an alumina pan.

In literature, mostly overestimated long-term thermal stabilities are reported, which are calculated from TGA-measurements by intersection of a straight baseline (in the low-temperature region without weight-loss) with the tangent of the weight versus temperature (in the high-temperature decomposition region) [26]. Decomposition already starts at temperatures far below this onset temperature [26–29]. Moreover, the sample is heated fast and extremely brief compared to long-term operation, also resulting in an overestimation of the temperature at which decomposition starts [26–29]. For a better understanding of the thermal decomposition of ionic liquids, more detailed information on the decomposition mechanism and kinetics is needed.

So far, only few attempts were made to analyze the thermal decomposition mechanism, the decomposition kinetics and the decomposition products of ILs. Chan et al. [30] found that 1-ethyl-3-methylimidazolium halide ILs decompose by an attack of the highly nucleophilic halide on the primary alkyl group (S_N2 reaction), with 1-ethylimidazole and methyl halide as the main products [31]. Therefore, imidazolium-based ILs decompose at lower temperatures in the presence of nucleophiles [32]. It was argued that branched alkyl groups are attacked by the halide via an S_N1 reaction, leading to lower decomposition temperatures [19]. Baranyai et al. [29] investigated the thermal decomposition mechanism of 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide ILs, and suggested degradation of the anion as possible thermal decomposition pathway, but the anion degradation products were not detected. Wooster et al. [33] found that pyrrolidinium ILs decompose under formation of *N*-alkyl pyrrolidine. Furthermore, it was found that bis(trifluoromethylsulfonyl)imide ILs undergo exothermic decomposition, whereas halide ILs decompose endothermically [13]. Kinetics of the thermal decomposition of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate were measured by Fox et al. [28].

The thermal decomposition mechanism and kinetics of most ILs are still unknown. A first reason is that the number of ILs is very large. Moreover, it is impossible to measure the thermal decomposition mechanism and kinetics of all ILs because the synthesis of a large variety of ILs is cumbersome and measurements are time-consuming and expensive. A tool to predict thermal decomposition properties of ILs on basis of their structure is desired. This tool should not only calculate a maximum operating temperature below which no thermal degradation occurs, but also indicate how rapidly an IL decomposes at a specific temperature (kinetics) and predict which decomposition products are formed (mechanism). So far, such a tool is non-existent.

In this work quantum chemical calculations will be used as tool to predict the thermal stability of ILs. This article aims to use the quantum chemical calculations (density functional

theory, B3LYP) only as a predictive tool for the decomposition reactions of ILs, and not to provide the highest accurate chemical structures of the ILs using the most advanced quantum chemical theory. Previously, we showed that quantum chemical calculations (density functional theory (DFT)) are a useful tool to predict the electrochemical stability of ILs [34]. Now, we will predict the thermal breakdown phenomena, including the type of thermal decomposition reactions and products that are formed under high temperatures, as well as the thermal decomposition temperatures of a variety of ILs. Moreover, the obtained mechanistic information gives insight into the reactivity of ILs with certain chemical compounds, such as the reactor construction material or the solute that is distilled from an IL. Finally, the height of the decomposition temperature determines whether an IL itself can be distilled albeit at very high temperatures and very low pressures, where ILs have a measurable vapor pressure [35]. All these issues are particularly important for the selection of a suitable IL for a specific high-temperature application.

2. Experimental

All calculations were carried out using the Spartan '04 molecular modeling suite of programs [36]. First, the IL structures were fully geometry-optimized using the semi-empirical PM3 method. Next to the equilibrium geometries, also the transition state geometries of the thermal decomposition reactions (the minimization of the maximum energy in all possible reaction pathways) were calculated with the PM3 method. Thereafter, all PM3 structures were used as input for full optimization at the B3LYP level (DFT), using the 6-31 G** basis set [37]. The B3LYP energies were used to calculate the activation energies of the decomposition reactions.

3. Results and discussion

In this work, the thermal decomposition mechanism and temperatures of several ILs are predicted using quantum chemical calculations at the B3LYP level. The structures and total energies of the ILs, the transition states and the products of the thermal decomposition reactions are calculated. The total energies are used to calculate the activation energy ΔE^a of the thermal decomposition reaction:

$$\Delta E^a = E_{\text{transition state}} - E_{\text{reactant 1}} - E_{\text{reactant 2}} - \dots \quad (1)$$

In principle, it is possible to predict the kinetics of the decomposition reaction from the activation energy ΔE^a . The simplest estimate for the reaction rate constant k_r of the thermal decomposition reaction is:

$$k_r = \left(\frac{k_B T}{h} \right) \exp \left(-\frac{\Delta E^a}{RT} \right) \quad (2)$$

wherein thermodynamic contributions are neglected, and k_B and h are the Boltzmann and Planck constants, respectively. A better prediction of the kinetics can be obtained using a more sophisticated quantum chemical approach for the pre-exponential factor. This will make the computational effort

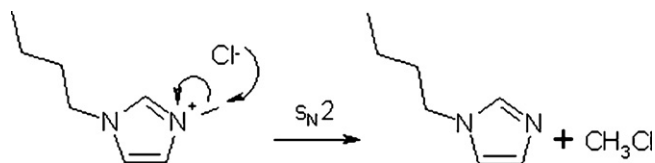


Fig. 1. Thermal decomposition of $[\text{bmim}^+][\text{Cl}^-]$ into methyl chloride and 1-butylimidazole ($\Delta E^a = 127 \text{ kJ/mol}$).

considerably larger, and thus the application as a fast tool for pre-optimization less attractive. We will show that B3LYP calculations are sufficient to predict the thermal decomposition mechanism and temperature of ILs, taking into account that previously measured experimental decomposition temperatures are not highly accurate due to their sensitivity to impurities.

3.1. Effect of type of anion on thermal decomposition

First, the effect of the anion of the IL on the thermal decomposition mechanism and kinetics is investigated. Using quantum chemical calculations, the ILs with highly nucleophilic anions, such as halides, were found to be thermally decomposing by dealkylation of the cation via an $\text{S}_{\text{N}}2$ reaction of the easiest accessible alkyl group, which is in agreement with experimental results [30]. For example, the IL 1-butyl-3-methylimidazolium chloride ($[\text{bmim}^+][\text{Cl}^-]$) decomposes into methyl chloride and 1-butylimidazole ($\Delta E^a = 127 \text{ kJ/mol}$), which is favored over the formation of butyl chloride and 1-methylimidazole ($\Delta E^a = 136 \text{ kJ/mol}$). This was also found in experiments [31]. Fig. 1 schematically shows the thermal decomposition mechanism of $[\text{bmim}^+][\text{Cl}^-]$ and Fig. 2 shows the corresponding energy profile. It can be seen that the thermal decomposition of $[\text{bmim}^+][\text{Cl}^-]$ is an endothermic reaction, which is consistent with experimental observation [13].

For the decomposition of the ILs 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}^+][\text{PF}_6^-]$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}^+][\text{BF}_4^-]$), two decomposition mechanisms seem to be possible. The first route involves the transfer of the proton

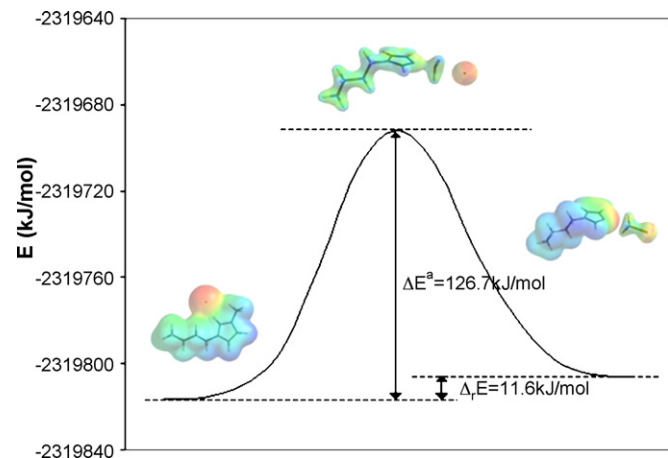


Fig. 2. Energy profile of the thermal decomposition of $[\text{bmim}^+][\text{Cl}^-]$ into methyl chloride and 1-butylimidazole.

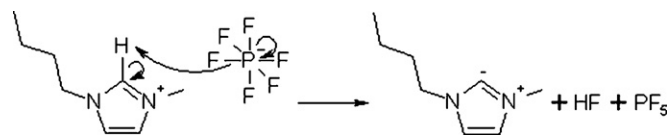


Fig. 3. Thermal decomposition of $[\text{bmim}^+][\text{PF}_6^-]$ into a 1-butyl-3-methylimidazolium carbene, HF and PF_5 ($\Delta E^a = 313 \text{ kJ/mol}$).

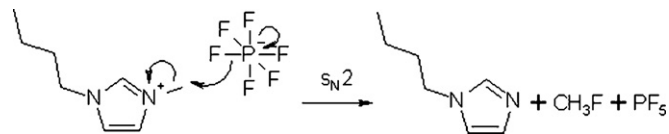


Fig. 4. Thermal decomposition of $[\text{bmim}^+][\text{PF}_6^-]$ into 1-butylimidazole, methyl fluoride and PF_5 ($\Delta E^a = 213 \text{ kJ/mol}$).

on the C2-position to the anion, resulting in the formation of a 1-butyl-3-methylimidazolium carbene, hydrogen fluoride and PF_5 or BF_3 (see Fig. 3). The carbene is not stable, but reacts via an addition reaction with the double bond of a second IL molecule. The proton transfer step is an endothermic reaction that does not show any transition state. The energy barrier for this reaction is calculated from the difference in energy level of the products and reactants and is very high. For example, the energy barrier for the decomposition of $[\text{bmim}^+][\text{PF}_6^-]$ via this route is as high as 313 kJ/mol , which is close to the upper limit of 347 kJ/mol for the breaking of carbon–carbon bonds in cracking reactions. Therefore, a decomposition mechanism with a smaller activation energy is more likely to occur.

The second possible route is the formation of 1-butylimidazole, methyl fluoride and PF_5 or BF_3 via an $\text{S}_{\text{N}}2$ -mechanism (see Figs. 4 and 5), which is favored over the formation of 1-methylimidazole and butyl fluoride (see previous paragraph). The activation barrier of the thermal decomposition of $[\text{bmim}^+][\text{PF}_6^-]$ via this route is only 213 kJ/mol , so this decomposition mechanism is favored. Also, for $[\text{bmim}^+][\text{BF}_4^-]$ the second route is preferred ($\Delta E^a = 195 \text{ kJ/mol}$) over the first route. The energy profiles of the thermal decomposition of $[\text{bmim}^+][\text{PF}_6^-]$ and $[\text{bmim}^+][\text{BF}_4^-]$ via the second route are shown in Figs. 6 and 7, respectively. It can also be noticed that the thermal decomposition of both ILs is highly endothermic, which is in agreement with experiments [13].

From Figs. 4 and 5 it can be concluded that thermal degradation of $[\text{bmim}^+][\text{PF}_6^-]$ and $[\text{bmim}^+][\text{BF}_4^-]$ in the absence of water does not lead to the formation of hydrogen fluoride. However, when water is added to the system (or present as impurity in the IL), the methyl fluoride will react with water under the formation of methanol and HF. This can be the reason for the experimental observation that HF is formed in $[\text{bmim}^+][\text{PF}_6^-]$ and $[\text{bmim}^+][\text{BF}_4^-]$ ILs at higher temperatures [1]. Finally,

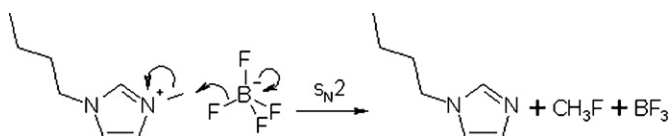


Fig. 5. Thermal decomposition of $[\text{bmim}^+][\text{BF}_4^-]$ into 1-butylimidazole, methyl fluoride and BF_3 ($\Delta E^a = 195 \text{ kJ/mol}$).

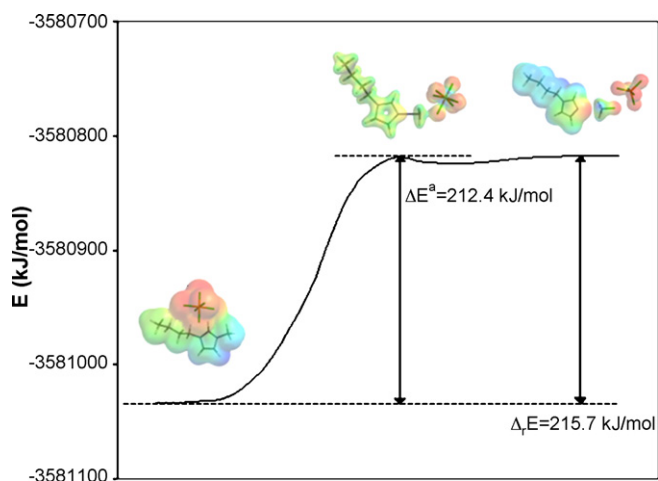


Fig. 6. Energy profile of the thermal decomposition of $[\text{bmim}^+][\text{PF}_6^-]$ into 1-butylimidazole, methyl fluoride and PF_5 .

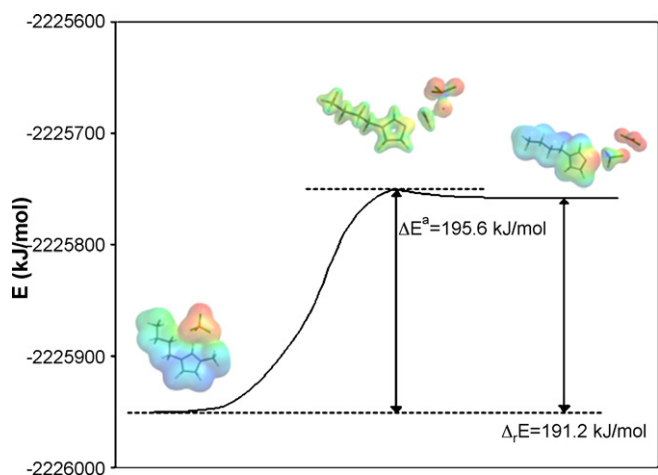


Fig. 7. Energy profile of the thermal decomposition of $[\text{bmim}^+][\text{BF}_4^-]$ into 1-butylimidazole, methyl fluoride and BF_3 .

it can be concluded that $[\text{bmim}^+][\text{PF}_6^-]$ and $[\text{bmim}^+][\text{BF}_4^-]$ have a better thermal stability (higher activation barrier) than $[\text{bmim}^+][\text{Cl}^-]$, which is in accordance with experiments [20].

Dicyanamide ILs also decompose via an $\text{S}_{\text{N}}2$ dealkylation. For example, the IL 1-butyl-3-methylimidazolium dicyanamide ($[\text{bmim}^+][\text{N}(\text{CN})_2^-]$) decomposes into 1-butylimidazole and methylated dicyanamide ($\Delta E^{\text{a}} = 160 \text{ kJ/mol}$), which is favored over the formation of 1-methylimidazole and butylated dicyanamide. Fig. 8 schematically shows the thermal decomposition mechanism of $[\text{bmim}^+][\text{N}(\text{CN})_2^-]$ and in Fig. 9 the corresponding energy profile is depicted. The thermal decomposition of $[\text{bmim}^+][\text{N}(\text{CN})_2^-]$ is a slightly endothermic reaction. From the height of the activation barrier it

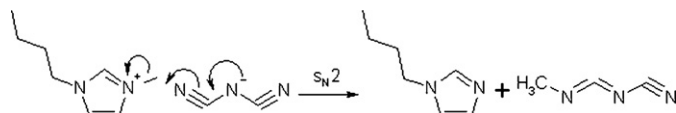


Fig. 8. Thermal decomposition of $[\text{bmim}^+][\text{N}(\text{CN})_2^-]$ into 1-butylimidazole and methylated dicyanamide ($\Delta E^{\text{a}} = 160 \text{ kJ/mol}$).

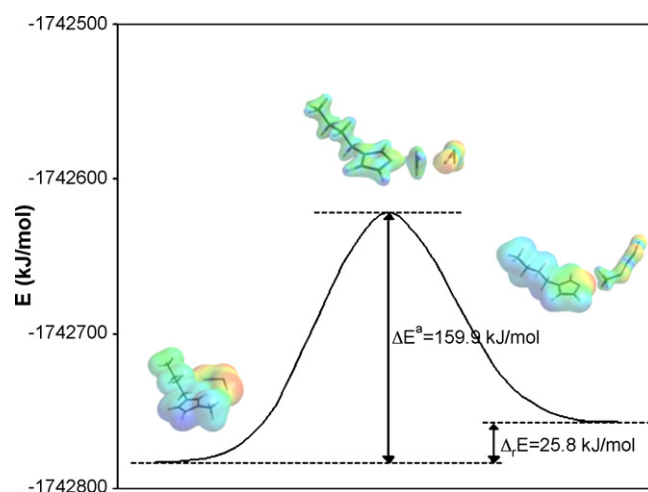


Fig. 9. Energy profile of the thermal decomposition of $[\text{bmim}^+][\text{N}(\text{CN})_2^-]$ into 1-butylimidazole and methylated dicyanamide.

can be noticed that $[\text{bmim}^+][\text{N}(\text{CN})_2^-]$ has a thermal stability higher than $[\text{bmim}^+][\text{Cl}^-]$, but lower than $[\text{bmim}^+][\text{BF}_4^-]$ and $[\text{bmim}^+][\text{PF}_6^-]$, which is in agreement with experimental results [14].

ILs that contain non-nucleophilic anions, such as the bis(trifluoromethylsulfonyl)imide anion, cannot decompose via dealkylation or proton transfer. According to the quantum chemical calculations, the lowest activation barrier reaction for the thermal breakdown of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{bmim}^+][\text{NTf}_2^-]$) is the degradation of the anion by sulfur dioxide release (the cation stays intact, see Fig. 10). This is in agreement with the results from Baranyai et al. [29] that suggest degradation of the anion as possible thermal decomposition pathway. The activation energy of this thermal decomposition is 255 kJ/mol , from which it can be concluded that $[\text{bmim}^+][\text{NTf}_2^-]$ is a more thermally stable IL than $[\text{bmim}^+][\text{Cl}^-]$, $[\text{bmim}^+][\text{BF}_4^-]$, $[\text{bmim}^+][\text{PF}_6^-]$ and $[\text{bmim}^+][\text{N}(\text{CN})_2^-]$. This was also found in experiments [14,15,20]. The energy profile of the thermal decomposition reaction is shown in Fig. 11. In contrary to the previously described thermal breakdown reactions, the thermal decomposition of $[\text{bmim}^+][\text{NTf}_2^-]$ is not an endothermic but an exothermic reaction, which is again in agreement with experiments [13].

Because only the anion of $[\text{bmim}^+][\text{NTf}_2^-]$ is degrading (the cation stays intact), the quantum chemical calculations were repeated for the anion only. Using this simplification, an activation energy of 260 kJ/mol was found, which is in close agreement with the 255 kJ/mol for the calculation in which the cation is included. Therefore, the anion approximation, which requires less computational effort, gives a reasonable estimate for the thermal decomposition of bis(trifluoromethylsulfonyl)imide

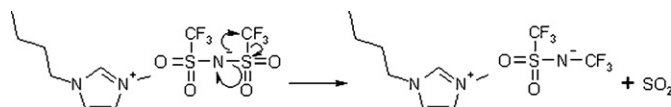


Fig. 10. Thermal decomposition of $[\text{bmim}^+][\text{NTf}_2^-]$ by sulfur dioxide release ($\Delta E^{\text{a}} = 255 \text{ kJ/mol}$).

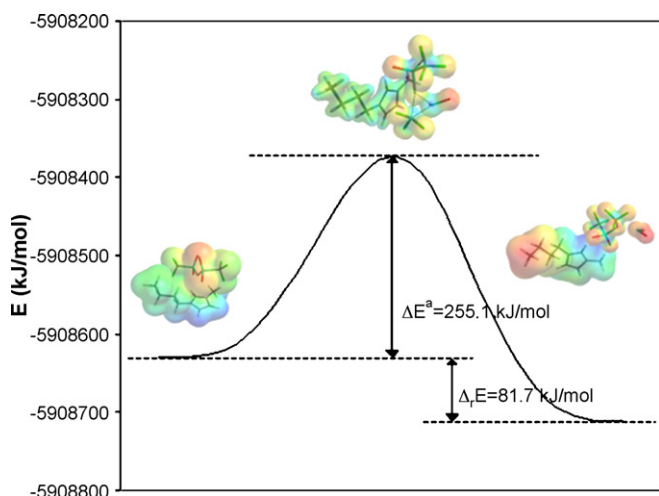


Fig. 11. Energy profile of the thermal decomposition of $[\text{bmim}^+][\text{NTf}_2^-]$ by sulfur dioxide release.

Table 1

Calculated activation barriers (this work) and experimentally determined thermal decomposition temperatures (from literature) for the thermal degradation of several 1-butyl-3-methylimidazolium ILs with different anion

IL	ΔE^a (kJ/mol)	T_{decomp} ($^{\circ}\text{C}$)	Ref.
$[\text{bmim}^+][\text{Cl}^-]$	127	254	[15]
$[\text{bmim}^+][\text{N}(\text{CN})_2^-]$	160	300	[14]
$[\text{bmim}^+][\text{BF}_4^-]$	195	361	[14]
$[\text{bmim}^+][\text{PF}_6^-]$	213	370	[24]
$[\text{bmim}^+][\text{NTf}_2^-]$	255	427	[25]

ILs.

In Table 1 an overview of the calculated activation energies and the experimentally determined thermal decomposition temperatures of several 1-butyl-3-methylimidazolium ILs with different anions is given. From Fig. 12 it can be seen that the correlation is excellent with a correlation coefficient of 0.99. Therefore, the quantum chemical calculations are able to pre-

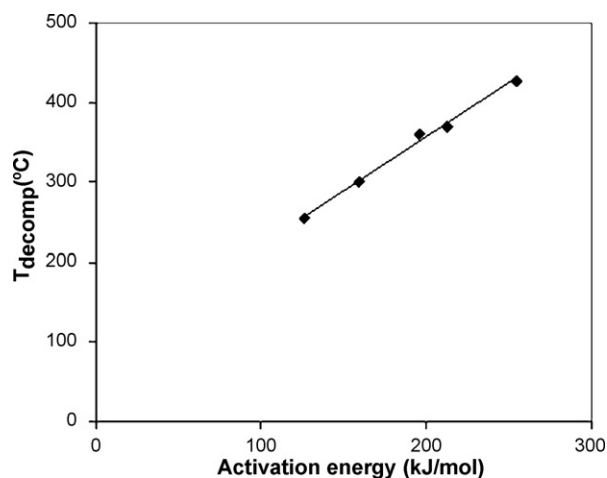


Fig. 12. Plot of the calculated activation energy (B3LYP method) of the most likely thermal degradation reaction versus the experimentally determined thermal decomposition temperature of the IL [14,15,24,25]. The correlation coefficient is 0.99.

dict the thermal stability of these ILs very well. However, using the most simple estimate for k_r (Eq. (2)) the quantum chemical calculations predict that ILs degrade at much lower temperatures ($\sim 100^{\circ}\text{C}$) than the experimentally TGA-determined thermal decomposition temperatures indicate. For example, the first order rate constant of the thermal degradation reaction of $[\text{bmim}^+][\text{BF}_4^-]$ ($\Delta E^a = 195$ kJ/mol) at a temperature of 265°C ($= 538$ K) is $1.0 \times 10^{-6} \text{ s}^{-1}$ (Eq. (2)), resulting in 0.1% conversion in 1000 s. This means that significant decomposition takes place well below the experimentally TGA-determined thermal decomposition temperature of 361°C [14]. Reason is that the TGA-measured onset decomposition temperatures are calculated by intersection of a straight baseline with the tangent of the weight versus temperature, so that some decomposition occurs at temperatures lower than this onset decomposition temperature, which was also previously found by other groups [26–29].

3.2. Effect of alkyl chain length of cation on thermal decomposition

Next, the effect of the chain length of the cation of the IL on the thermal decomposition temperature is investigated. Therefore, the activation energies of the thermal breakdown reactions of several 1-alkyl-3-methylimidazolium chloride ILs with different alkyl chain groups (ethyl, propyl, butyl, hexyl and octyl) were calculated. The results are shown in Table 2. As can be seen from Table 2, the effect of the alkyl chain length on the thermal decomposition temperature is very small, which is in agreement with experimental results [13–15,25]. In all cases, the formation of methyl chloride and 1-alkylimidazole via an $\text{S}_{\text{N}}2$ -mechanism (see Fig. 1) was preferred over the formation of alkyl chloride and 1-methylimidazole, because the activation barrier was always ~ 10 kJ/mol lower. This was also found in experiments [31].

3.3. Effect of type of cation on thermal decomposition

Finally, the effect of the type of cation on the thermal decomposition mechanism and kinetics has been investigated. Therefore, the thermal degradation reactions of several tetrafluoroborate ILs with different cation are predicted. Using quantum chemical calculations, pyridinium-based ILs were found to be thermally decomposing by dealkylation of the cation via an $\text{S}_{\text{N}}2$ reaction. For example, the IL 1-butylpyridinium tetrafluorob-

Table 2

Calculated activation barriers (this work) and experimentally determined thermal decomposition temperatures (from literature) for the thermal degradation of several 1-alkyl-3-methylimidazolium chloride ILs with different alkyl chain length

IL	ΔE^a (kJ/mol)	T_{decomp} ($^{\circ}\text{C}$)	Ref.
$[\text{emim}^+][\text{Cl}^-]$	126	261	[13]
$[\text{pmim}^+][\text{Cl}^-]$	125	261	[13]
$[\text{bmim}^+][\text{Cl}^-]$	127	254	[15]
$[\text{hmim}^+][\text{Cl}^-]$	128	253	[15]
$[\text{omim}^+][\text{Cl}^-]$	128	254	[15]

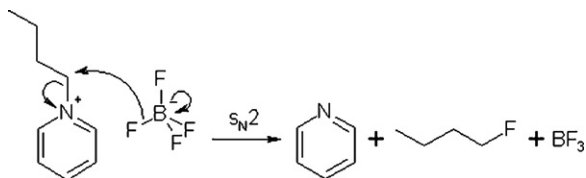


Fig. 13. Thermal decomposition of $[\text{bpy}^+][\text{BF}_4^-]$ into pyridine, butyl fluoride and BF_3 ($\Delta E^a = 134 \text{ kJ/mol}$).

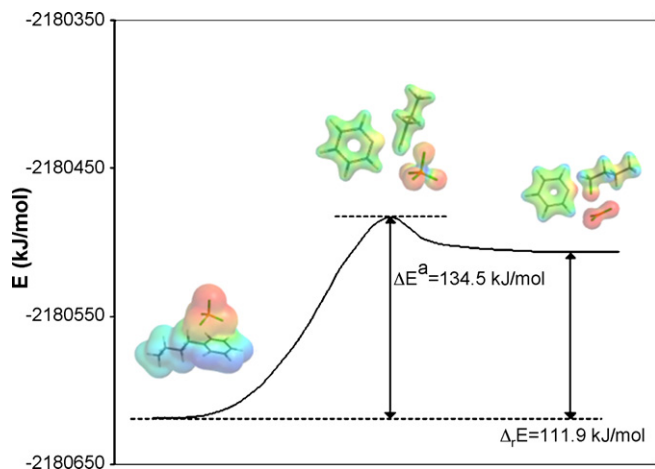


Fig. 14. Energy profile of the thermal decomposition of $[\text{bpy}^+][\text{BF}_4^-]$ into pyridine, butyl fluoride and BF_3 .

orate ($[\text{bpy}^+][\text{BF}_4^-]$) decomposes into pyridine, butyl fluoride and BF_3 ($\Delta E^a = 134 \text{ kJ/mol}$). Fig. 13 schematically shows the thermal decomposition mechanism of $[\text{bpy}^+][\text{BF}_4^-]$ and Fig. 14 shows the endothermic energy profile of the thermal decomposition reaction. Although the thermal decomposition temperature of $[\text{bpy}^+][\text{BF}_4^-]$ is unknown, it was previously found that pyridinium-based ILs are less stable than imidazolium-based ILs [21,23], which is in agreement with the lower calculated activation energy for the thermal decomposition of $[\text{bpy}^+][\text{BF}_4^-]$ ($\Delta E^a = 134 \text{ kJ/mol}$) compared to $[\text{bmim}^+][\text{BF}_4^-]$ ($\Delta E^a = 195 \text{ kJ/mol}$).

Dialkylpyrrolidinium-based ILs also decompose via an $\text{S}_{\text{N}}2$ dealkylation reaction. For example, the IL 1,1-butylmethylpyrrolidinium tetrafluoroborate ($[\text{bmpyrrol}^+][\text{BF}_4^-]$) decomposes into 1-butylpyrrolidine, methyl fluoride and BF_3 ($\Delta E^a = 144 \text{ kJ/mol}$), which is favored over the formation of 1-methylpyrrolidine, butyl fluoride and BF_3 , the formation of 1-methylpyrrolidine, butene and HBF_4 (E2-elimination), and the formation of a tertiary amine as a result of a ring opening reaction. This is in agreement with the results of Wooster et al. [33]. In Fig. 15 the thermal decomposition mechanism is presented,

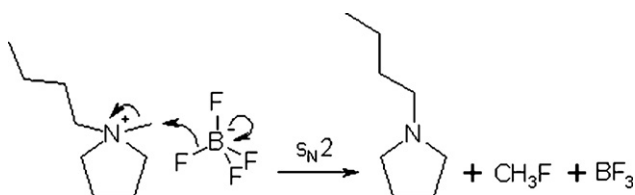


Fig. 15. Thermal decomposition of $[\text{bmpyrrol}^+][\text{BF}_4^-]$ into 1-butylpyrrolidine, methyl fluoride and BF_3 ($\Delta E^a = 144 \text{ kJ/mol}$).

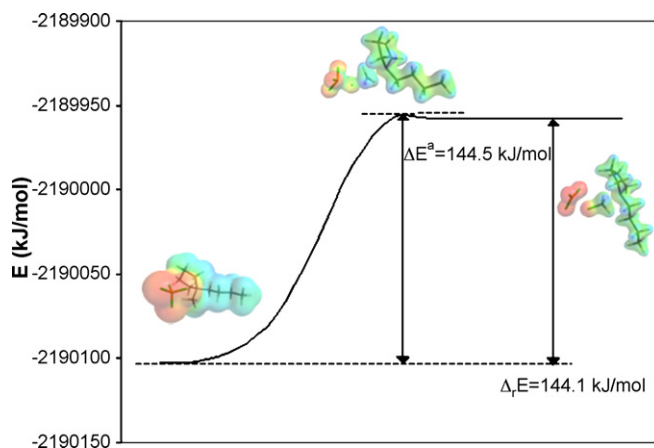


Fig. 16. Energy profile of the thermal decomposition of $[\text{bmpyrrol}^+][\text{BF}_4^-]$ into 1-butylpyrrolidine, methyl fluoride and BF_3 .

and Fig. 16 shows the calculated energy profile. From the height of the activation barrier it can be noticed that $[\text{bmpyrrol}^+][\text{BF}_4^-]$ has a higher thermal stability than $[\text{bpy}^+][\text{BF}_4^-]$, but a lower thermal stability than $[\text{bmim}^+][\text{BF}_4^-]$, which is in agreement with the experimental observation that pyrrolidinium-based ILs are more stable than pyridinium-based ILs, but less stable than imidazolium-based ILs [22,23]. Moreover, from Fig. 16 can be concluded that the thermal decomposition of $[\text{bmpyrrol}^+][\text{BF}_4^-]$ is highly endothermic.

Imidazolium-based ILs that are substituted with a methyl group on the C2-position were experimentally found to be more thermally stable due to the removal of the acidic hydrogen [14,19,22–24]. However, using quantum chemical calculations it was found that the IL 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($[\text{bdmim}^+][\text{BF}_4^-]$) does not decompose at the C2-position, but via a dealkylation reaction at one of the nitrogen atoms, resulting in the formation of 1-butyl-2-methylimidazole, methyl fluoride and BF_3 (similar to the decomposition of $[\text{bmim}^+][\text{BF}_4^-]$, see Fig. 5). In fact, the activation energy of the thermal decomposition reaction of $[\text{bdmim}^+][\text{BF}_4^-]$ is even lower ($\Delta E^a = 182 \text{ kJ/mol}$) than that of $[\text{bmim}^+][\text{BF}_4^-]$ ($\Delta E^a = 195 \text{ kJ/mol}$). Therefore, a lower thermal stability of $[\text{bdmim}^+][\text{BF}_4^-]$ compared to $[\text{bmim}^+][\text{BF}_4^-]$ is expected according to the quantum chemical calculations. The reason for the experimental observation that $[\text{bdmim}^+][\text{BF}_4^-]$ actually decomposes at higher temperatures is most likely the result of the presence of water in the IL, which is generally present as an impurity in the IL. When the acidic hydrogen on C2-position is replaced by a methyl group, the acid-catalyzed reaction of water with methyl fluoride (leading to the formation of HF) will proceed slower, thus resulting in a more stable IL. However, $[\text{bdmim}^+][\text{BF}_4^-]$ will decompose faster than $[\text{bmim}^+][\text{BF}_4^-]$ when no water is present in the IL.

Finally, the thermal decomposition mechanism and activation energy of tetraalkylammonium and tetraalkylphosphonium ILs was investigated. It was found that both types of ILs decompose into the trialkyl-form via an $\text{S}_{\text{N}}2$ -mechanism that is energetically favored over an E2-elimination reaction. For example, the IL tetraethylammonium tetrafluoroborate

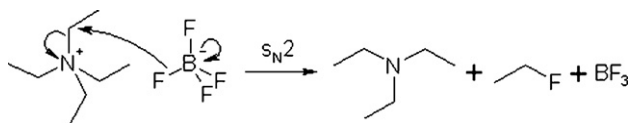


Fig. 17. Thermal decomposition of $[N2222^+][BF_4^-]$ into triethylamine, ethyl fluoride and BF_3 ($\Delta E^a = 151$ kJ/mol).

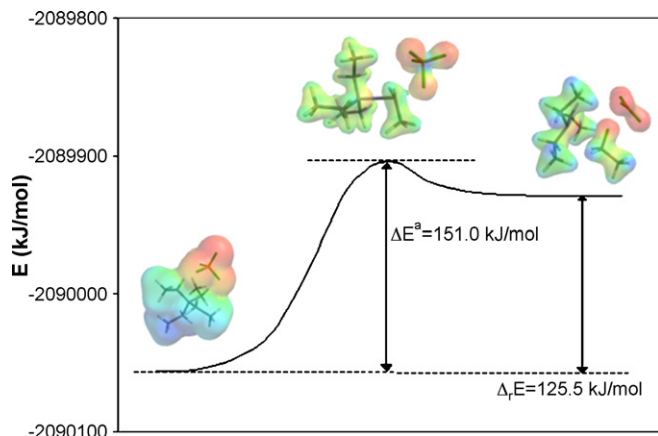


Fig. 18. Energy profile of the thermal decomposition of $[N2222^+][BF_4^-]$ into triethylamine, ethyl fluoride and BF_3 .

$[N2222^+][BF_4^-]$ decomposes into triethylamine, ethyl fluoride and BF_3 ($\Delta E^a = 151$ kJ/mol), which is shown in Fig. 17. Fig. 18 shows the energy profile. In the same way, the IL tetraethylphosphonium tetrafluoroborate ($[P2222^+][BF_4^-]$) decomposes into triethylphosphine, ethyl fluoride and BF_3 ($\Delta E^a = 204$ kJ/mol). Both thermal breakdown reactions are highly endothermic, which is in agreement with experiments [13]. On basis of the height of the activation barriers can be concluded that the ammonium-based IL has a lower stability than imidazolium-based ILs, whereas the phosphonium-based IL has a higher stability. This was also found in experiments [22,23].

An overview of the calculated activation energies of several tetrafluoroborate ILs with different cations can be found in Table 3. Although the TGA-determined thermal decomposition temperatures of these ILs are unknown, the trend in thermal stability is also observed in experiments [13,21–23], except for the experimentally determined higher stability of $[bdmim^+][BF_4^-]$ compared to $[bmim^+][BF_4^-]$, which has been related to the reaction of $[bmim^+][BF_4^-]$ with water.

Table 3

Calculated activation barriers for the thermal degradation of several tetrafluoroborate ILs with different cation

IL	ΔE^a (kJ/mol)
$[bpy^+][BF_4^-]$	134
$[bmpyrrol^+][BF_4^-]$	144
$[N2222^+][BF_4^-]$	151
$[bdmim^+][BF_4^-]$	182
$[bmim^+][BF_4^-]$	195
$[P2222^+][BF_4^-]$	204

4. Conclusions

Quantum chemical calculations are an excellent tool to predict the thermal stability of ILs. The effects of anion, cation and alkyl chain length on the thermal decomposition mechanism and kinetics can be investigated and correlated with experimental results. Using quantum chemical calculations it is possible to find the most probable decomposition mechanism, as well as the activation energy of the decomposition reaction. The calculated activation energy corresponds well with the measured decomposition temperature and may be used to predict the decomposition temperature of an ionic liquid before it is synthesized.

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