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Thermal stability of imidazolium-based ionic liquids

Léa Chancelier[a], Olivier Boyron[a], Thibaut Gutel[b], Catherine C. Santini[a*]

[a] *UMR CNRS 5265, C2P2, University of Lyon, 43 bd du 11 novembre 1918, F-69100 Villeurbanne*

[b] *CEA, LITEN, 17 rue des martyrs, F-38000 Grenoble*

catherine.santini@univ-lyon1.fr

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This work highlights the factors tuning the thermal stability of imidazolium-based ionic liquids (IL) associated to bis(trifluoromethanesulfonyl)imide anion [NTf_2]. The decomposition temperatures (T_d) are evaluated by thermogravimetric analyses (TGA) with optimised parameters to obtain reproducible T_d. The impact of the alkyl chain length and of the presence of functional groups and unsaturations on T_d are evaluated. The thermal behavior is governed by Van der Waals interactions between alkyl chains, and by inter and intra coulombic interactions such as hydrogen bonds.

Introduction

Ionic liquids (IL) are defined as molten salts, liquid at room temperature or at least below 100 °C. Such low melting points result from the association of an organic cation with delocalised charge to a weakly coordinating organic or inorganic anion.[1] The combination of a broad variety of cations and anions theoretically allows to form as many as 10^6 IL. Hence, a wide diversity in IL structure is possible, and by modifying either the cationic or the anionic component of an IL, their physical properties such as melting point, viscosity, thermal stability, solubility and hydrophobicity can easily be fine-tuned.[2, 3]

Due to the quite strong coulombic interactions within these substances, IL fulfill all conditions required by green solvents. Unlike most organic solvents, they do not evaporate unless heated to the point of thermal decomposition, typically 200-300 °C.[1] They have flash points higher than 200 °C and can be considered as flame retardants.[4-8] In addition to this very interesting combination of properties, they are excellent solvents which may be immiscible with water or organic solvents affording biphasic systems with them. Moreover, they may exhibit very large electrochemical windows. Keeping in mind the principles of green chemistry, IL have attracted much attention in the scientific community (chemists, biologists, and others) during the past two decades.[1, 9] They have consequently been considered for a variety of applications such as separation technology,[10, 11] catalysis,[12-14] biomass treatment[15, 16] and energy storage.[1, 9, 17, 18]

For industrial applications of IL as alternative green solvents, the determination of both decomposition and melting temperatures is of paramount importance. These properties determine the liquid range of the compounds, and consequently their range of application.

Among all IL, we focused our study on the imidazolium-based IL [C_1C_nIm], Figure 1, as these cations can be easily chemically modified.[1, 9, 19] The T_d of typical imidazolium-based IL are collected in Table 1.

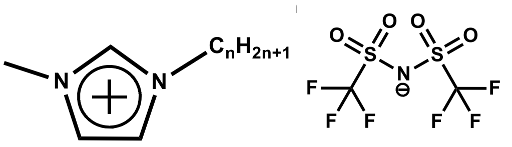

Figure 1. Alkylmethylimidazolium cation [C_1C_nIm] and bis(trifluoromethanesulfonyl)imide anion [NTf_2]

Table 1. T_d values of typical IL depending on cation and anion natures. The onset temperatures are reported in roman font and start temperatures in italic type. Bold characters stand for inert atmosphere (nitrogen or argon), and the data are underlined depending on the heat rate as follow: 5 °C.min^{-1}, 10 °C.min^{-1}, 20 °C.min^{-1} and no underlining when not available. C_1C_nIm: 1-alkyl-3-methylimidazolium; $C_1C_1C_n$Im: 1-alkyl-2,3-dimethylimidazolium cation, and $C_1C_1C_1C_1C_1$Im: 1,2,3,4,5-pentamethylimidazolium cation

T_d (°C)	**Cl**	**BF_4**	**PF_6**	**NTf_2**
C_1C_1Im				**444**[20]
C_1C_2Im	278[21] **281**[22]	300[23] 445[24] **447**[25] **450**[22] **450**[26]	***190***[27] **273**[27] **481**[22]	280[28] 358[29] 374[30] **400**[31] **410**[32] **411**[33] **419**[34] **439**[20] **453**[22]
C_1C_3Im	**269**[35] **281**[22]	**393**[35] **435**[25] **450**[26]	**440**[22]	**453**[22]
C_1C_4Im	***150***[36] *173*[37] **193**[38] 202[37] **234**[32] **254**[39] **264**[36] **268**[35] 291[21]	**280**[40] ***290***[36] 300[28] **361**[36] **380**[35] **403**[39] 424[24] **425**[41] **435**[25] **450**[26]	300[28] 315[42] **433**[41] **349**[39]	275[28] ***330***[36] **391**[43] **422**[36] **423**[41] **427**[20] **439**[39] 461[21]
C_1C_5Im	**262**[35]	**408**[35]		
C_1C_6Im	**253**[39]	***262***[44] **425**[44]	***320***[44] **417**[39] **454**[44]	275[28] ***302*** [44] **428**[20] **461**[44]
C_1C_8Im	**243**[39]		**376**[39]	*>300*[45] **425**[20]
C_1C_{16}Im	**230**[32]			
$C_1C_1C_2$Im	**290**[22]		**500**[22]	**456**[22]
$C_1C_1C_3$Im	**260**[32] **284**[22]	**390**[32] 457[24]	**399**[22]	***385***[36] **462**[22] **462**[36]
$C_1C_1C_4$Im	**257**[32]	***285***[36] **347**[38] **364**[46] **380**[36] **398**[46] **405**[32] **428**[46]	***235***[36] **347**[38] **373**[36] **425**[32]	
$C_1C_1C_{10}$Im	**239**[32]	**400**[32]	**420**[32]	
$C_1C_1C_{16}$Im	**239**[32]	**400**[32]	**400**[32]	
$C_1C_1C_{20}$Im		**390**[32]		
$C_1C_1C_1C_1C_1$Im			**487**[22]	**466**[22]

The T_d of these imidazolium-based IL are mainly dependent on the nature of the anion. Whatever the cation, halide-derivated IL always show the lowest T_d, and fluorinated anions show the highest.[47-51] The observed stability order is: $NTf_2 > PF_6 \geq BF_4 > Cl$, Table 2. IL containing weakly coordinating anions (less nucleophilic) are generally the most stable.[1, 52-54] The most common decomposition mechanism is the formation of alkyl-halide species by S_N1 and S_N2 nucleophilic substitution mechanisms,[55, 56] underlining the importance of the size, the basicity and the nucleophilicity of the anion. The IL stability is consequently inversely proportional to the stability of these alkyl-halides.[49, 52, 57]

This work is focused on NTf_2 anion, also called TFSI, BTA or TFSA, Figure 1, affording liquid products at room temperature in most cases. Furthermore, it provides high thermal stability and its hydrophobicity allows efficient purification by removal of salts in water, which is required *e.g.* for lithium-ion batteries application.[1] This anion also prevents from HF generation observed with BF_4 or PF_6 anions in the presence of water.[57] Note that the decomposition of NTf_2 anion is exothermic, and releases SO_2 gas.[57]

Stability orders
$PF_6 > BETI > NTf_2 \approx BF_4 \gg I \approx Br \approx Cl$[22]
$OTf > BF_4 > PF_6 > Br > NO_3$[54]
$NTf_2 > PF_6 > BF_4$[44]
$NTf_2 = OTf > dca > SCN$[45]
$NTf_2 > OMs \approx Tcm \approx dca$[58]
$NTf_2 > PF_6 > BF_4 > OMs > OTf > I > Cl$[47]
$BF_4 > Cl \sim I$[35]

Table 2. Stability orders of different anions associated to imidazolium cations; dca: $N(CN)_2$, Tcm: $C(CN)_3$

It is admitted that due to their extremely low vapor pressure, the upper limit of liquid range of IL is their T_d.[1] T_d are generally determined by thermogravimetric analysis (TGA) where the mass of a sample is monitored during an increase of temperature (with constant heating rate), in a controlled atmosphere. The mass loss is related to the formation of volatile species which are extracted by the gas flow. Thus, T_d are determined only when such species are formed during the decomposition of the product. Another limit is the possible IL vaporisation, influencing also the mass loss, which is detrimental for protic IL and IL containing volatile anion such as acetate.[59, 60]

In this work, we performed temperature-ramped or scanning TGA, for which T_d value is known to vary significantly with experimental conditions including heating rate, carrier gas nature and flow rate, pan nature and sample purity. Thus, only T_d determined under identical experimental conditions can be compared.[4, 24, 36, 46, 61-64] *e.g.* in the literature the value of onset T_d of 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide $[C_1C_4Im][NTf_2]$ varies by more than 150 °C, Table 3.

T_d (°C)	275	**391**	**422**	**427**	**427**	**439**	461
Ref.	[28]	[43]	[36]	[20]	[a]	[39]	[21]

Table 3. Decomposition temperatures reported in the literature for [C_1C_4Im][NTf_2]; [a] this work; 5 °C.min^{-1}, 10 °C.min^{-1} or 20 °C.min^{-1}, no underlining when unspecified; **bold** for inert gases (N_2 and Ar)

This discrepancy results from the use of different definitions of T_d and different experimental parameters. In order to compare T_d of different IL, we standardize the experimental parameters. Firstly, the possible definitions of T_d (start, onset and peak temperatures) are explained. Then the major experimental parameters affecting T_d values are optimised in order to obtain reproducible T_d. Once the set of parameters are selected, the evolution of T_d with the nature of the alkyl chain linked to imidazolium ring is studied.

Results and discussion

1. Experimental parameters for TGA

1.1. Decomposition temperatures definitions

Several definitions for decomposition temperatures (T_d) are reported, including start, onset, x% mass loss, and peak temperatures. The *start temperature* (T_{start}) is the temperature at which the sample starts to lose mass.[36] It is the temperature at which the first derivative of the weight loss *vs* temperature |dw/dT| is superior to 10^{-4} mg.s^{-1}. The associated uncertainty is 5 °C. The x% *mass loss temperature* is the temperature at which 1%, 5% or 10% of the mass are lost.[30, 32, 34, 43, 65-67] The *peak temperature*, or peak mass loss temperature, is defined as temperature at which the first derivative of the mass *vs* temperature is the highest. This analysis gives results even up to 80 °C higher than onset temperatures.[46]

The *onset temperature* (T_{onset}) is generally defined by the tangent method, but also by the 5% mass loss temperature.[4, 46, 68] In the first case, T_{onset} is determined by the intersection of two lines, by using a software or manually. The first one is a straight baseline along the temperature axis (in the low-temperature region with no weight-loss), and the second is the tangent of the mass *vs* temperature curve as decomposition occurs (in the high-temperature region).[24, 36, 47, 57] The reliability of the onset temperature is estimated at 5 °C from determining the tangents.[36, 44, 46, 69, 70]

In the literature, the disparity between these different definitions is well stated and it is admitted that thermal degradation occurs well before the T_{onset} based on tangents method.[46, 62, 64, 71] The definitions and the corresponding values for start, onset and peak temperatures in the case of [C_1C_4Im][NTf_2] are illustrated in Figure 2.

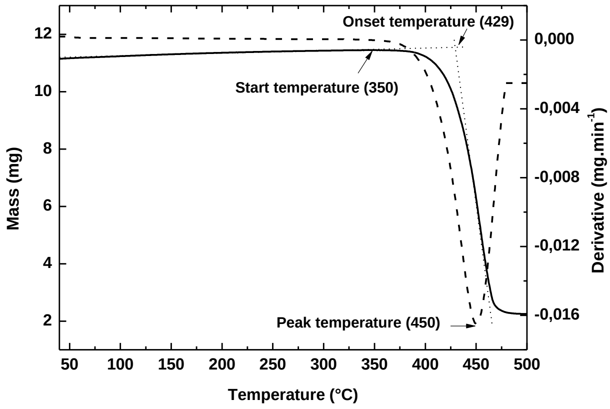

Figure 2. Comparison of the T_d values of $[C_1C_4Im][NTf_2]$ (5 °C.min^{-1}, argon flow) according to the definitions T_{onset}, T_{start} and T_{peak}; full line represents the sample mass and dashed line represents the first derivative

1.2. Heat rate

In TGA experiments the heat rate can vary from 1 to 20 °C.min^{-1}.[22, 35, 61, 72] For very slow rates the observed degradation can overlap long term degradation processes. Contrarily, high heat rates lead to an overestimation of T_d. This explains the difference of *ca* 50 °C between T_{onset} of $[C_1C_4Im][NTf_2]$ at different heat rates, being equal to 418 °C at a heating rate of 2 °C.min^{-1}, while it is 427, 443 and 473 °C at heating rates of 5, 10 and 20 °C.min^{-1}, respectively. The trend is also observed for $[C_1C_1C_4Im][BF_4]$ or $[C_1C_2Im][NTf_2]$ IL.[3, 46, 53] We choose a rate of 5 °C to provide a good estimation of the T_{start} in reasonable experimental times.

1.3. Pan nature

Several pan materials like aluminum,[24, 66, 75, 76] platinum,[22, 36, 46, 72, 74, 77, 78] and ceramic[4, 24, 48] can be used to run TGA experiments. They can be sealed (in the case of aluminum) or open. The difference between alumina and aluminum pans is minor (less than 5 °C) for almost all the IL.[22] But in some specific cases, NTf_2 anions induce corrosion of aluminum collectors used for Li-ion batteries.[77, 78] We choose to use aluminum pans easily prepared and sealed in an argon-filled glovebox.

1.4. Atmosphere

A large variety of gases can be used such as nitrogen,[20, 22, 25, 27, 35, 36, 44, 63, 64, 66, 69, 73, 79-83], argon,[26, 67, 75, 76, 84, 85], helium,[34] and air.[37, 61, 86, 87] Employing different inert gases such as Ar or N_2 induces a slight change on the T_d values,[32, 65, 72] while air or oxygen lowers the T_d.[32, 61, 88] The TGA experiments are carried out under argon, and the gas flow is set to 30 mL.min^{-1}.

1.5. Sample mass

The mass of the sample for TGA experiments is reported from 5 to 40 mg, typically corresponding to one drop of ionic liquid.[34, 46, 69, 73-75, 83, 85] For a same product *e.g.* $[C_1C_4Im][BF_4]$, TGA performed on a 13 or 30 mg sample can lead to a T_d difference of up to 50 °C (at 10 °C.min^{-1} under air).[61] This change may be due at least in part to the instrument type, specifically to the position of the thermocouple relatively to the sample.[61] To improve the heat diffusion through the sample and to avoid uneven heating,[74] low mass samples are preferred. The T_d modification is not significantly observed on

$[C_1C_4Im][NTf_2]$ (> 2 °C) with our protocol, most probably due to the lower heat rate. In all our experiments the sample mass is set to 10 ± 3 mg.

1.6. Purity

Traces of impurities such as residual starting materials or salts (Li^+, Na^+) strongly affect T_d.[89-91] Less than 1 w% of water do not alter T_d,[46, 72] while even with highly hydrophobic IL higher water concentrations deeply lower T_d, *e.g.* of 45 °C for $[C_1C_4Im][NTf_2]$.[39] In order to remove water, IL are stirred and heated under high vacuum for one or two days, affording a water amount varying from 1 to 2 000 ppm, Table 4.

Drying conditions			**Water content (ppm)**
Temperature (°C)	**Duration (h)**	**Pressure (mbar)**	
60 then 120	2 then 20	n.a.	< 1[92]
80 then 120	12 then 24	10^{-5}	< 10[93]
120	< 48	n.a.	< 17.5[76]
100	n.a.	n.a.	< 20[22]
65	48	n.a.	< 20[89]
80	48	10^{-3}	< 50[94]
100	24	n.a.	< 50[95, 96]
25	48	10^{-5}	< 60, this work
60	overnight	n.a.	1 000[97]
70	12	n.a.	< 2 000[85]
60	48	1	n.a.[69, 70]

Table 4. Influence of the drying duration, pressure and temperature on the IL water content; n.a.: not available

1.7. Selected experimental parameters

From the above results, all our results presented in the following part are compared under identical conditions. The TGA samples containing 10 ± 3 mg of purified and dried IL are prepared in aluminum sealed pans in an argon-filled glovebox, and the measurements are performed at 5 °C.min^{-1} under argon. The start decomposition temperature is defined as the temperature at which |dw/dT| > 10^{-4} mg.s^{-1}.

2. Playing around imidazolium cation

2.1. Mechanisms of Im-IL decomposition

Imidazolium-based IL degradation occur through different mechanisms, the main one being the loss of alkyl chains.[49, 53, 57, 98, 101] For example the nucleophilic substitution (S_N2) of the alkyl group by the anion (reverse Menschutkin reaction) is reported,[21, 32, 35, 49, 52, 55-57, 100-102] as well as Hofmann elimination yielding alkenes from the break of the N-C bond, Figure 3.[21, 37, 64, 98, 101] The terminal alkene is formed, and different isomers of the alkenes can be obtained after rearrangements.[32, 103-105] Also N-heterocyclic carbene (NHC) at the C_2 position can be formed due to the presence of an acidic proton, Figure 4.[32, 103-105] The opening of the cation ring occurs at much higher temperatures.[32, 106]

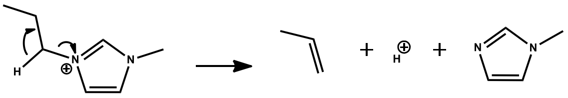

Figure 3. Hofmann elimination [37, 64, 98, 101]

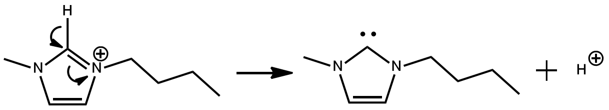

Figure 4. Formation of N-heterocyclic carbene NHC [32, 103-105]

2.2. Alkyl chain effects

The impact of the nature of the alkyl chain is studied varying their length and their substitution by alkyl chains, heteroatoms or unsatured groups.

2.2.1. Alkyl chain length

The T_{onset} and T_{start} evolutions of $[C_1C_nIm][NTf_2]$ in function of *n* (number of carbon atoms varying from 2 to 18) are depicted in Figure 5.

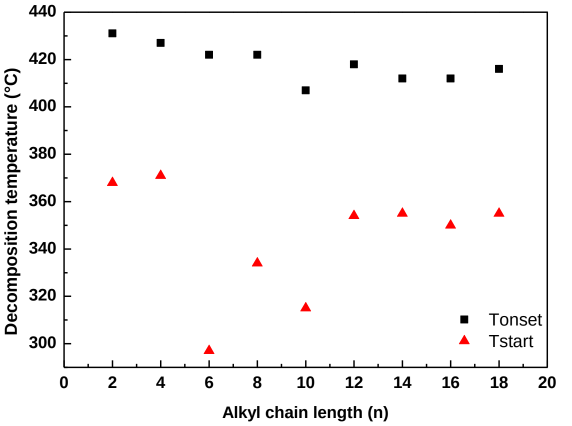

Figure 5. Influence of the alkyl chain length on the T_{onset} and T_{start} for $[C_1C_nIm][NTf_2]$

For these alkyl systems, in addition to H-bond network between anions and cations, simulation and experimental results report side-chain aggregation when n > 4, but no aggregation for shorter chains. These systems form of a continuous tridimensional network of ionic channels, coexisting with nonpolar domains.[107, 108] The size of these nonpolar domains is found linear with the alkyl chain length (~ 2.1 Å), and Van des Waals interactions between these alkyl chains increase of ~ 4.7 kJ.mol^{-1} per CH_2 group.[109]

From $[C_1C_1Im]$ to $[C_1C_4Im]$, the decomposition temperature (T_d) decreases with the molecular mass of the IL.[3, 20, 25, 28, 32, 102] For these short alkyl chains (*i.e.* with a C_n length ~ 4 Å), the charge-rich region is localised on imidazolium ring and the probability of alkyl chain segregation is weak.[107, 108, 110] These IL are mainly structured through electrostatic and hydrogen-bond interactions, leading to the formation of charge ordering over two or three coordination shells.[108]

When *n* increases from 4 to 6 carbons (*i.e.* length C_n ~ 5.5 Å), T_{start} decreases sharply, resulting from two factors. First, when *n* increases a breakdown in the symmetry of imidazolium ring is observed. Secondly, the longer alkyl chains constitute better leaving groups (more stable carbocations and carbon radicals).[102] Note that T_d as others physical constants *e.g.* heat capacity display a similar trend shift with $[C_1C_6Im][NTf_2]$.[107, 111-113]

For $[C_1C_nIm]$ containing longer alkyl chains (n > 6), T_d increases though the longer alkyl chains are better leaving groups,[45] in particular with *n* varying from 10 to 18 (length C_n ~ 12 Å). This result may be related to higher van der Waals interactions with long alkyl-chains.[40, 107-109, 114]

2.2.2. Asymmetric $[C_1C_{2n}Im][NTf_2]$ *vs* symmetric $[C_nC_nIm][NTf_2]$

The symmetric dialkylsubstituted imidazolium such as $[C_6C_6Im][NTf_2]$ decomposes at higher temperature than $[C_4C_4Im][NTf_2]$, from a larger carbon number as observed with asymmetric substituted IL (*vide supra*). Nevertheless

$[C_4C_4Im][NTf_2]$ and $[C_6C_6Im][NTf_2]$ have lower T_d than their asymmetric IL counterparts, with a comparable total number of carbons in the alkyl chains, $[C_1C_8Im][NTf_2]$ and $[C_1C_{12}Im][NTf_2]$ respectively, Figure 6.

Likewise, the volatility of $[C_nC_nIm][NTf_2]$ IL is significantly higher than for $[C_1C_{2n}Im][NTf_2]$ counterparts.[111] This observation is attributed, from the small- and wide- angle X-ray scattering (SWAXS) measurements, to the steric hindrance stemming from the symmetric chains connected to the cations which tend to separate the stacked imidazolium rings more than in the case of asymmetric cations.[111] This steric hindrance can confirm a lower T_d of $[C_nC_nIm][NTf_2]$ as compared to $[C_1C_{2n}Im][NTf_2]$, Figure 6.

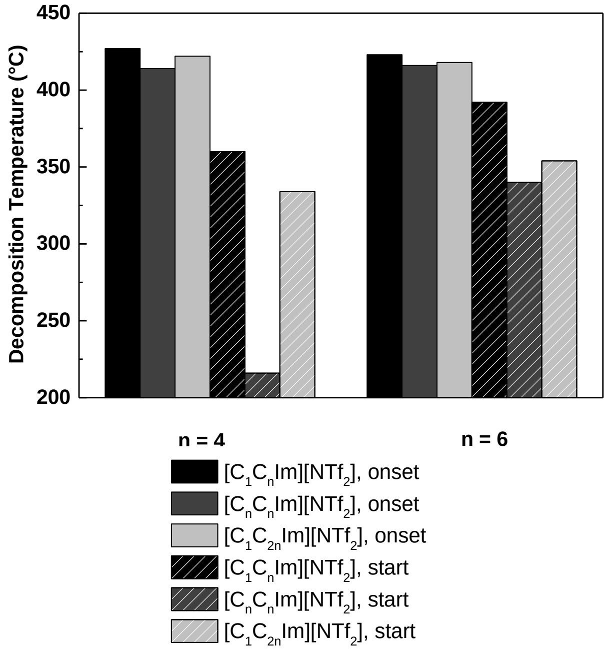

Figure 6. Effect of the symmetry of alkyl chains on T_d of several $[Im][NTf_2]$-based IL

2.2.3. Linear *vs* branched alkyl chains

The $[C_1C_3Im][NTf_2]$ IL with branched alkyl chains shows a lower T_d than the linear analogous (453 *vs* 409 °C).[22] Indeed, the branched alkyl chains increases the cation volume, inducing a higher disorder in the structure, separating the stacked imidazolium rings and lowering intramolecular electrostatic interactions. Moreover, branched alkyl chains are better leaving groups, affording more stable carbocations and carbon radicals, favoring the decomposition reaction (*vide supra*).[32, 35]

2.2.4. C_2-H substitution

No obvious T_d difference is observed between $[C_1C_nIm][NTf_2]$ and $[C_1C_1C_nIm][NTf_2]$ (1-alkyl-2,3-dimethylimidazolium), with n = 4 and 6.[4, 22, 32] The substitution of the other acidic protons to form $[C_1C_1C_1C_1C_1Im]$ (5 methyl groups on imidazolium ring) leads to minor increase of the T_d.[47] However, the potential formation of NHC, Figure 4, limits their thermal stability with time and in the presence of any basic substrate, Figure 7.[7, 115-117]

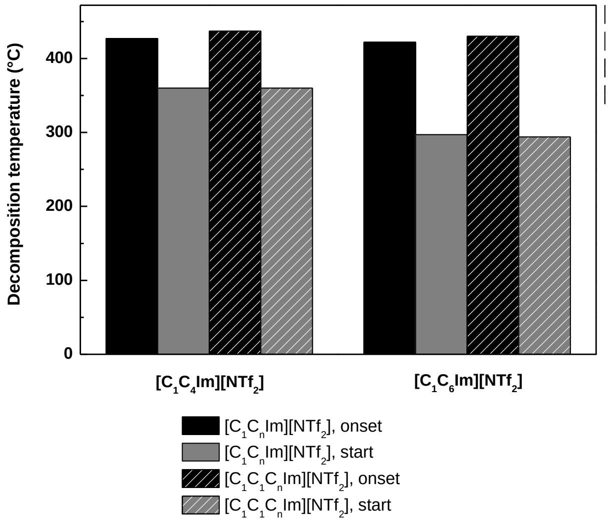

Figure 7. Effect of the C_2-H substitution of imidazolium-based IL on their T_d; this work

2.2.5. Alkyl chain functionalization

2.2.5.1. Fluoroalkyl *vs* alkyl chains

The fluorinated chains induce a T_d decrease compared to the alkyl analogous, Table 5. This can be explained by higher repulsion between fluoroalkyl chains, since the magnitude of the C-F bond dipole moment is 1.4 D *vs* 0.4 D for C-H bonds.[118, 119] This intermolecular repulsion tends to separate the stacked imidazolium rings, and contributes to a higher volatility of fluoroalkanes *vs* alkanes, and lower T_d values.[119-121]

Ionic liquid	T_{onset} (°C)
1,3-dibutylimidazolium [C_4C_4Im]	414
1-(3,3,4,4,4-pentafluorobutyl)-3-butyl imidazolium [$C_4C_{4f}Im$]	390
1,3-dihexylimidazolium [C_6C_6Im]	416
1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-hexylimidazolium [$C_6C_{6f}Im$]	390

Table 5. Effect of the fluorination of alkyl chains of imidazolium-based IL on their T_d, this work

2.2.5.2. Unsaturations

IL containing unsaturated chains are generally less stable than their saturated counterparts, Figure 8. Adding a second unsaturation generally lowers even more the stability,[26, 122] except for benzyl (CH_2-Ph)-derived IL due to the aromaticity and π-stacking of the C_6H_5 cycle.[45] The T_d of alkyne-functionalised IL is lower than the alkene-functionalised IL, *e.g.* T_d of 1-allyl-3-methylimidazolium bromide is 253 °C *vs* 192 °C for 1-propargyl-3-methylimidazolium bromide. The T_d lowering can be related to the presence of an H-bond (Br···H-$C_{acetylene}$) in the propargyl one, reducing the strength of the H-bonds between anion and the C_2-H of the cation and consequently the interconnection of the 3D-structure of IL.[123, 124]

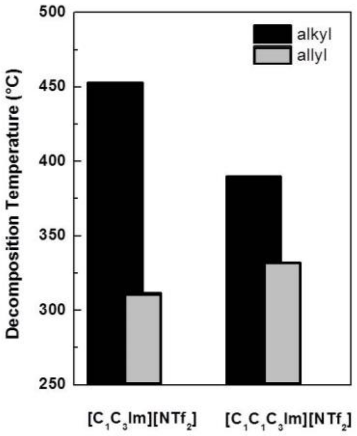

Figure 8. Effect of the presence of allyl group on different types of IL; [C_1C_3Im][NTf_2], this work; [$C_1C_1C_3Im$][NTf_2], [32, 67]

2.2.5.3. Functionalised IL

The T_d of a series of imidazolium-IL with alkyl chain length functionalised with cyano, ether or hydroxyl groups are reported in Figure 9 and Table 6.

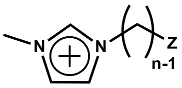

Figure 9. Functionalised imidazolium IL where Z can be OH, CN or CH_3 group

T_{start} (°C)	Alkyl	Cyano	Alcohol
n = 2	368[a]	303[a]	368[a]
n = 4	371[a]	361[a]	
n = 6	297[a]	373[a]	318[a]

Table 6. Influence of the functional groups on the T_{start} of [NTf_2]-IL; [a] this work

For short alkyl chains, *i.e.* n ≤ 4, the thermal stability is lowered by the addition of functional groups. For example changing from [$C_1(CH_2CH_3)Im$] to [$C_1(CH_2CN)Im$] cation decreases the T_{onset} from 278 °C[21] to

251 °C[125] (Δ = -27 °C) when associated to chloride anion, from 275 °C[56] to 210 °C[22] (Δ = -65 °C) with $[N(CN)_2]$ anion, and from 431 °C to 406 °C with $[NTf_2]$ anion, this work. The same tendency is detected with hydroxyl- and ether-functionalised IL, *e .g.* $[C_1C_1((CH_2)_2O(CH_2)_2)Im][NTf_2]$ decomposes at 405 °C while the T_d of $[C_1C_1C_4Im][NTf_2]$, is 430 °C.[126] Adding other alkoxy groups in the chain lowers T_d, Figure 10.[2, 34, 66, 126-130]

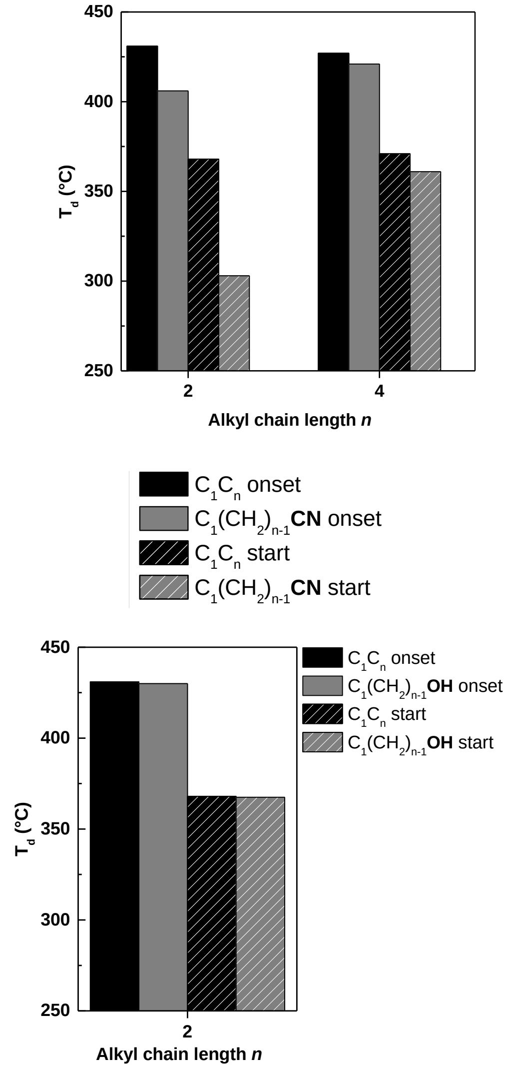

Figure 10. Influence of the presence of a cyano (left) or hydroxyl (right) group on T_d for short alkyl chains ($n \leq 4$)

The negative effect of the presence of a function on T_d can be explained by the formation of H-bonds between functional moieties (C≡N or O) and the C_2-H proton of imidazolium ring. These H-bonds (enthalpy value of 3.4 $kcal.mol^{-1}$) are evidenced through X-ray diffraction, Infrared and Raman spectroscopies, and density functional theory in IL based on $[C_1(CH_2CH_2OH)Im]$ and $[(CH_2CH_2OH)_2Im]$.[131] These interactions reduce the strength of the H-bonds between $[NTf_2]$ and the C_2-H, inducing lower T_d for IL containing functional groups ($[C_1C_2Im][NTf_2]$ decomposes at 431 °C, this work, *vs* 395 °C for $[(CH_2CH_2OH)_2Im][NTf_2]$).[68].

At the opposite, for the longer chains, higher T_{start} are observed for the functionalised chains (cyano and hydroxyl) compared to alkyl analogues T_d increases from 422 °C for $[C_1C_6Im][NTf_2]$ to 428 °C for $[C_1((CH_2)_5CN)Im][NTf_2]$, Figure 11.

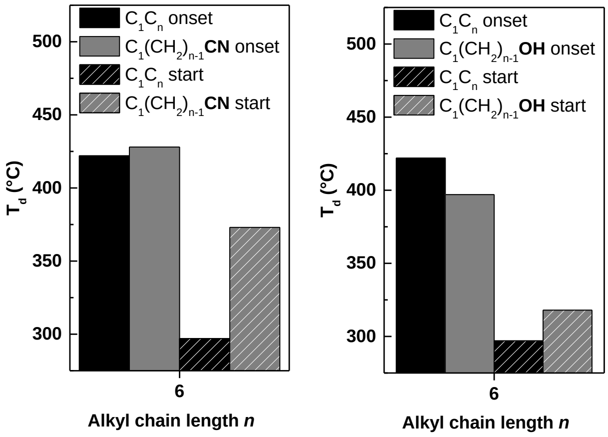

Figure 11. Influence of the presence of a cyano or hydroxyl group on T_d for long alkyl chains, this work

This trend can be explained by enhanced Van der Waals intermolecular interactions in longer chains. Furthermore with ether-based IL, a stronger interaction between the cations and the lone electron pairs of oxygen atoms can induce a wrapping of the chain around the cation protecting the imidazolium ring from nucleophilic attacks, leading to higher stability.[132, 133]

Conclusions

The objective of this work is to determine the factors influencing thermal stability of imidazolium-based ionic liquids associated to bis(trifluoromethanesulfonyl)imide anion [NTf_2]. Their decomposition occurs *via* nucleophilic substitution, Hofmann elimination or NHC formation. For these postulated mechanisms, both the natures of the anion and of the side chains of the cation have a crucial impact. From a perusal of the literature data and from our results, we postulate that the thermal stability of these IL is mostly controlled by structural and kinetic factors.

IL thermal stability is ruled by intermolecular interactions. The three most important ones are H-bonds, occurring between hydrogen and heteroatoms from anion or functionalised cation, coulombic interactions between anionic and cationic charges, and Van der Waals interactions between the side chains of the imidazolium rings. When the substitution of the alkyl chain induces a higher molecular volume of the cation, or the presence of Fluor atom, the T_d decreases. High T_d are induced by strong coulombic or van der Waals interactions, strong H-bond between anion and C_2H, or by high symmetry. The more stable IL are thus constituted of linear and short alkyl chains, with no functional groups, *i.e.*[C_1C_2Im].

Experimental part

The ionic liquids are synthesised and characterised after purification as already reported in the literature.[7, 31, 134] Before TGA analyses, all IL are vacuum-dried at room temperature for 48 h under high vacuum (10^{-5} mbars) and stored in an argon-filled glovebox. Their impurity levels are then measured. Their water content is lower than 60 ppm (mass ratio), as assessed by Karl Fisher coulometric titration, 831 Coulometer Metrohm. The chloride content is lower than 0.5 % as assessed by high resolution mass spectroscopy, close to 100 ppm as measured by elementary analysis. Thermal characterisations are performed with a Mettler Toledo TGA/DSC1 thermobalance equipped with an auto-sampler and a DSC heat flow measurement for simultaneous detection of enthalpy events. Indium and aluminium are used for the temperature calibration.

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