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Thermal Stability and Thermal Decomposition Mechanism of Imidazolium-based Ionic Liquids

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Arbeitskreis Thermophysik, Würzburg, 17./18.03.2014

DFG SPP: Material Synthesis in IL

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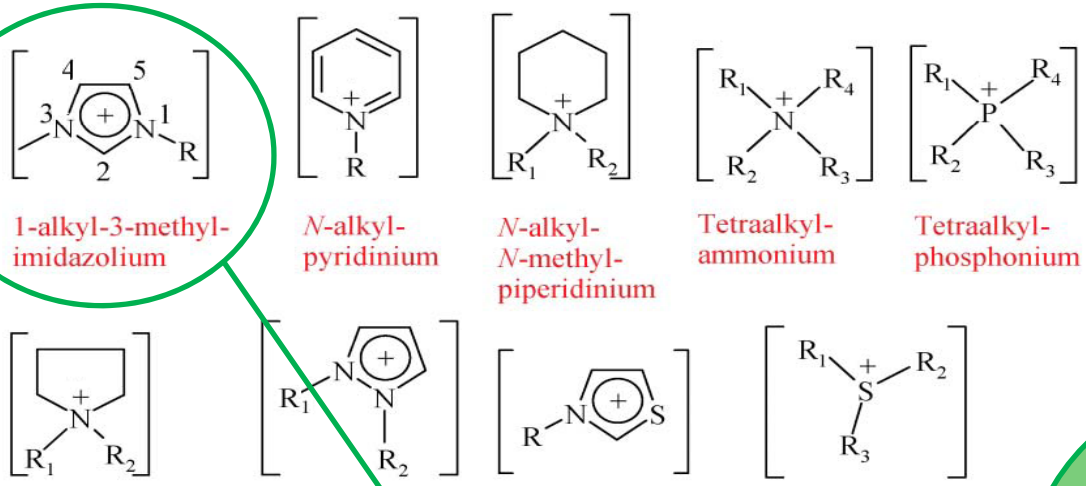
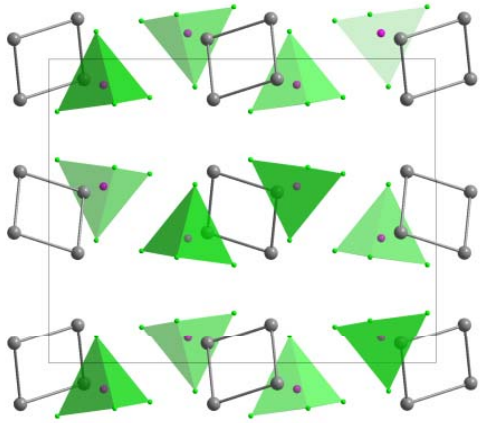
Most commonly used cations:



$R_{1,2,3,4} = CH_3(CH_2)_n$, ($n$ = 1, 3, 5, 7, 9); aryl; *etc.*

Some possible anions:

water-immiscible		water-miscible
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[NTf_2]^-$	$[OTf]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$	$[N(CN)_2]^-$	Br^-, Cl^-, I^-



Elements and compounds of group 15 and 16

Supercooling and Glass formation

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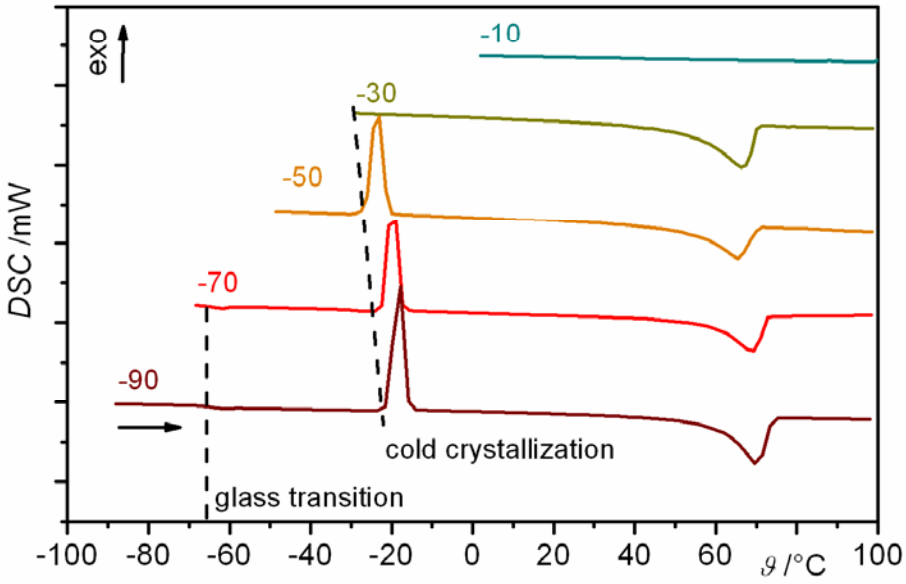
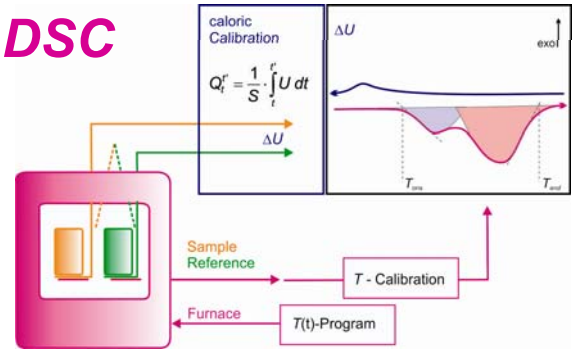
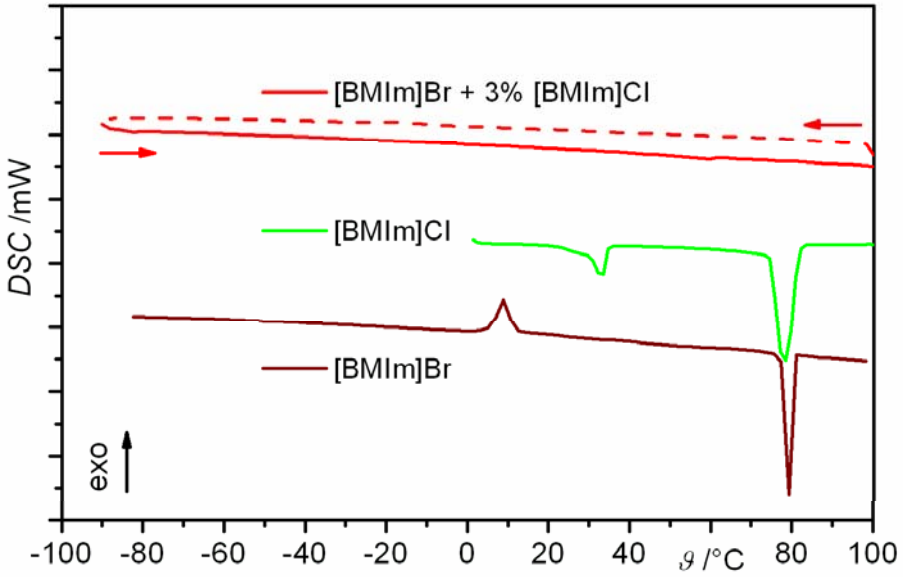


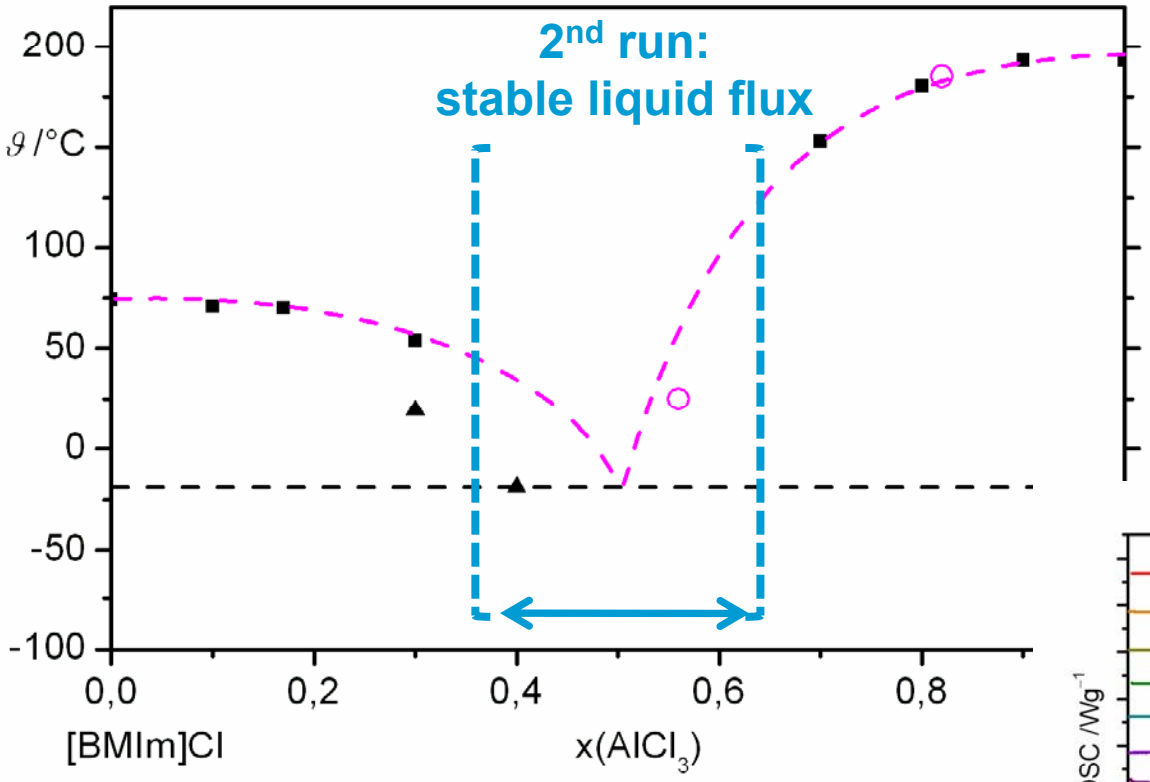
DSC

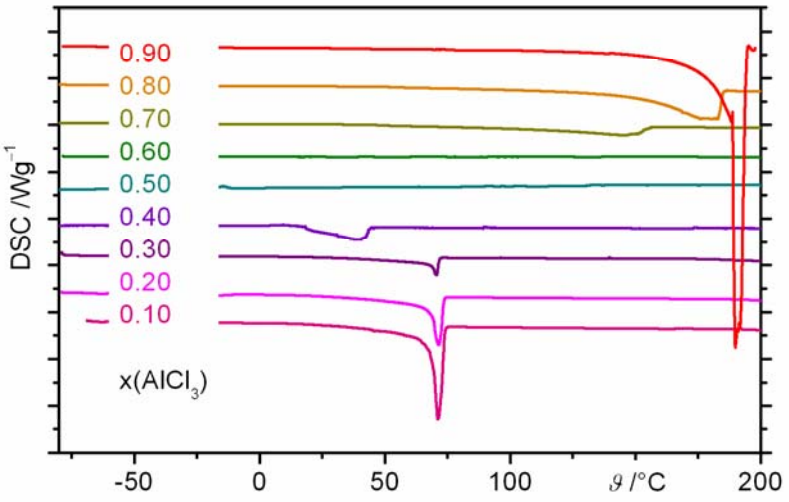




[BMIm]*X* (***X*** = **Cl**, **Br**)

Ionic liquid flux systems





x **[BMIm]Cl + (1−*x*) $AlCl_3$**

Phase Formation Processes

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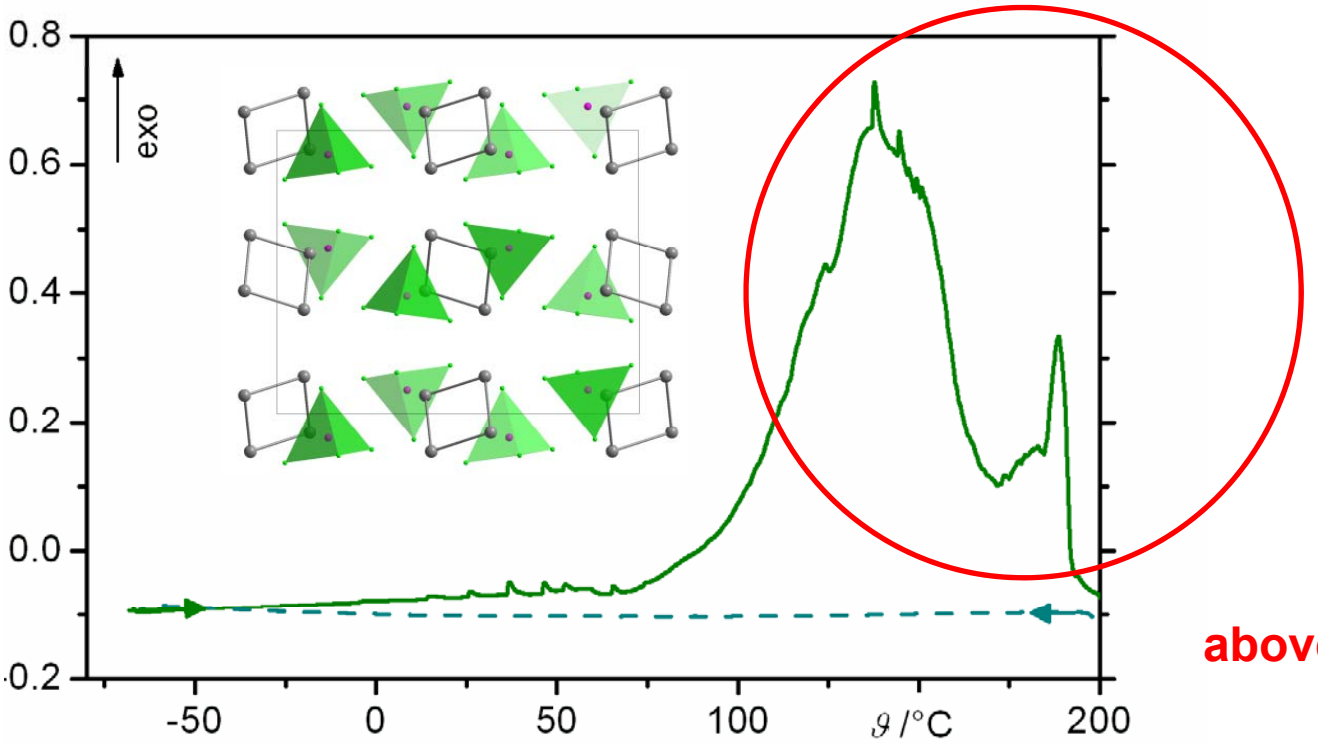


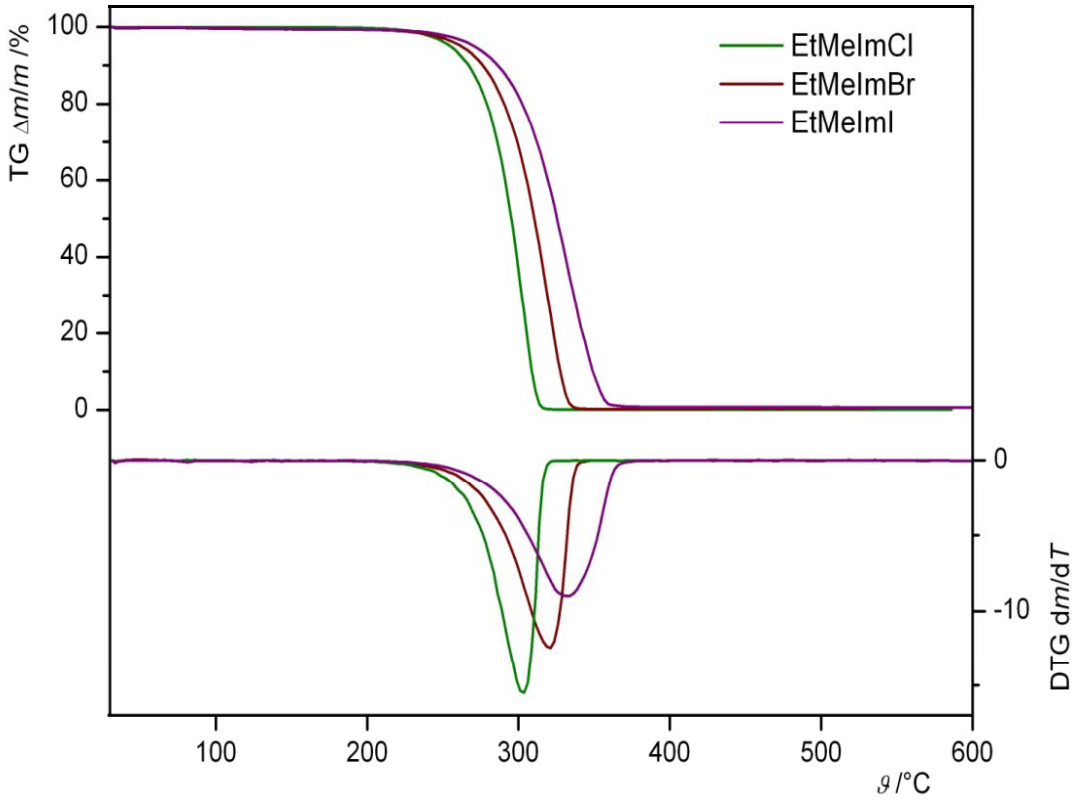
reactivity
above room temperature

Phase formation:

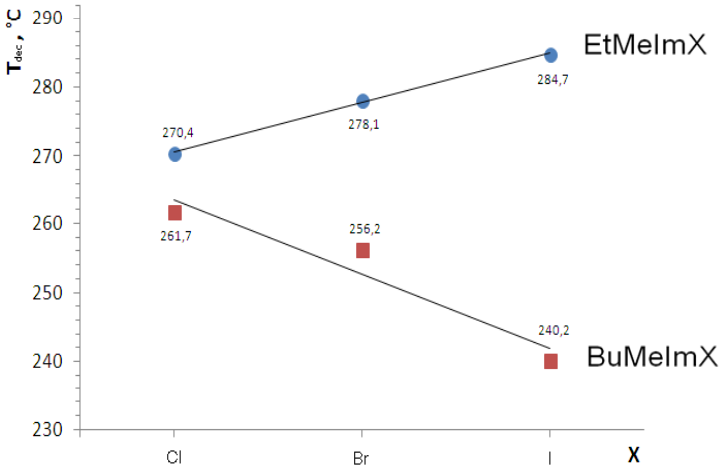
$7Te + TeCl_4 + 4AlCl_3 \rightarrow 2[Te_4](AlCl_4)_2$

Thermal stability
of ionic liquid at T ≈ 200 °C?

THERMAL STABILITY – TG



Substance	$T_{dec.}$, °C
EtMeImCl	270
EtMeImBr	278
EtMeImI	285
BuMeImCl	262
BuMeImBr	256
BuMeImI	240



THERMAL STABILITY – TG/MS

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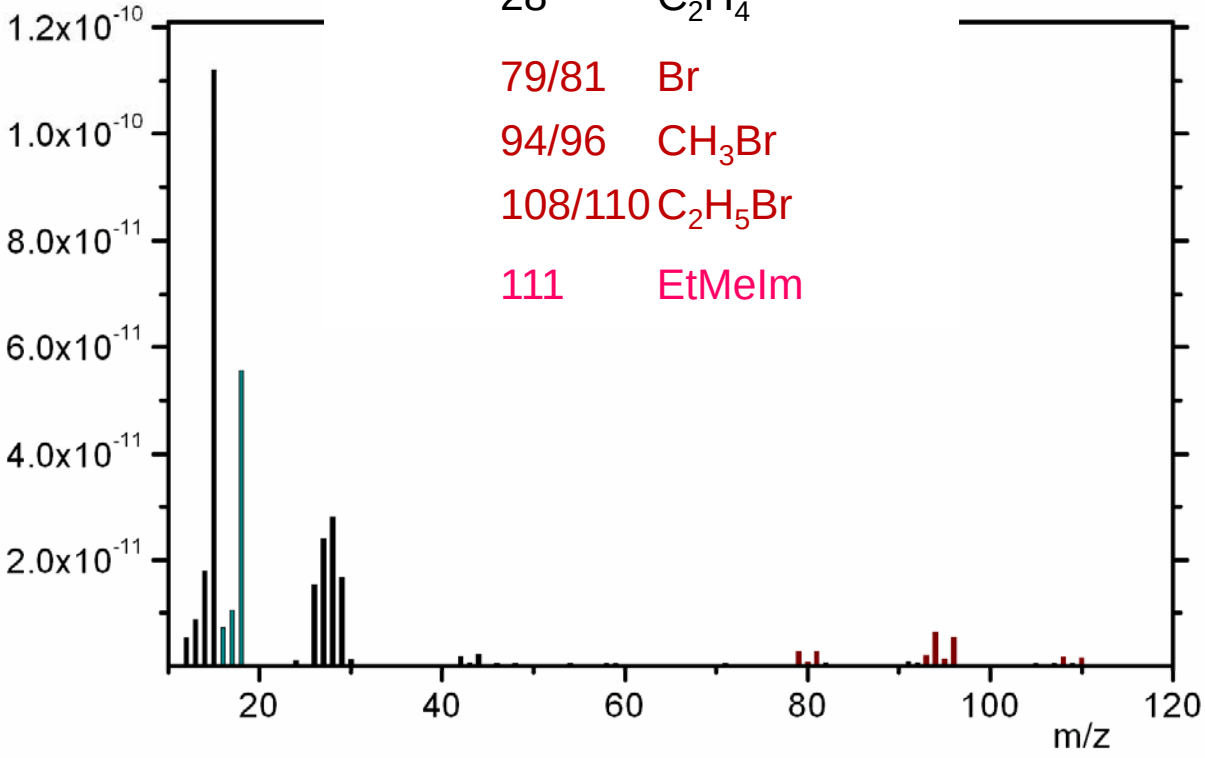
m/z =		
	15	CH_3
	17	NH_3
	28	C_2H_4
	79/81	Br
	94/96	CH_3Br
	108/110	C_2H_5Br
	111	EtMeIm

and fragments…



Mechanism of Decomposition

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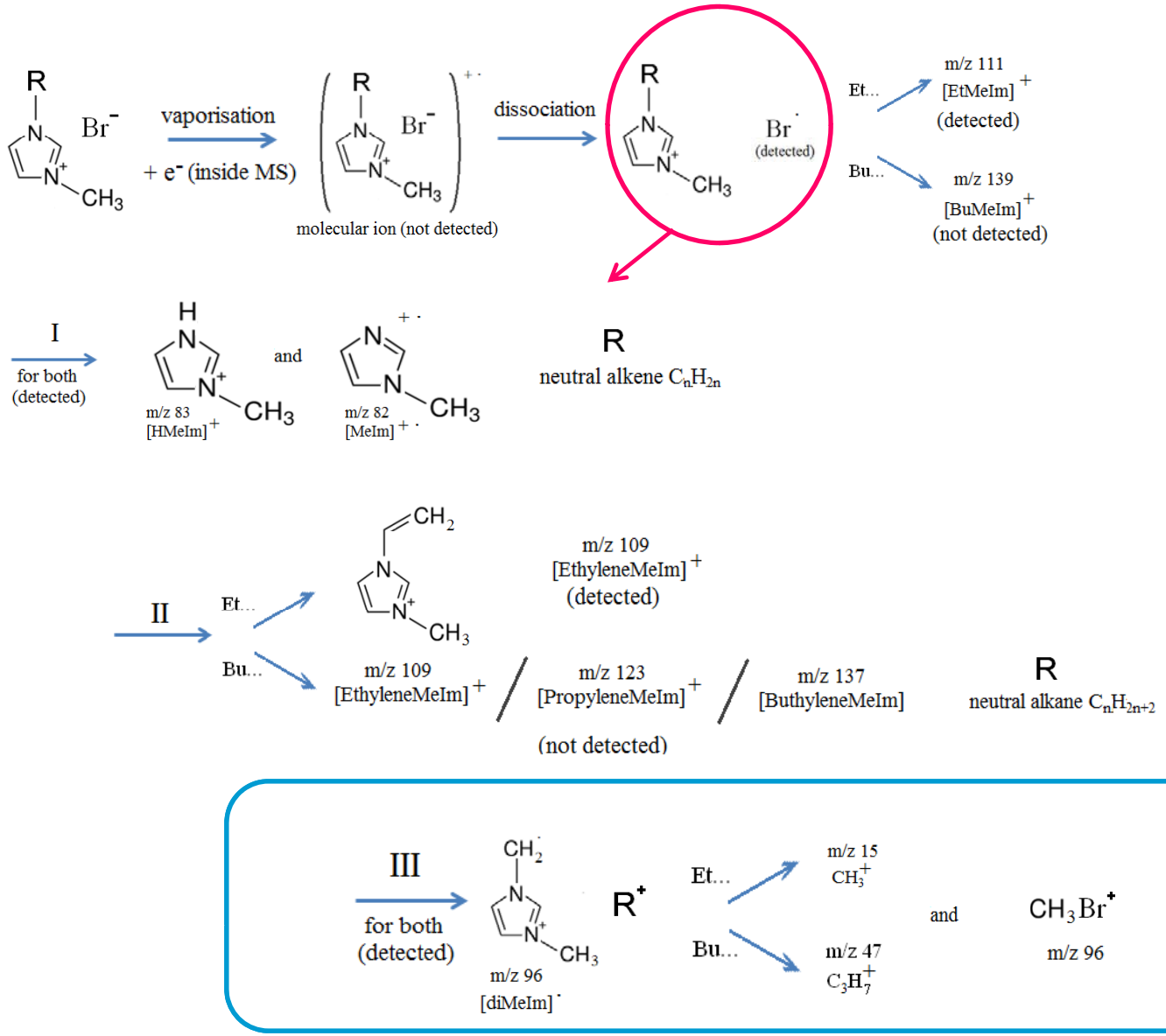

Mechanism of Decomposition

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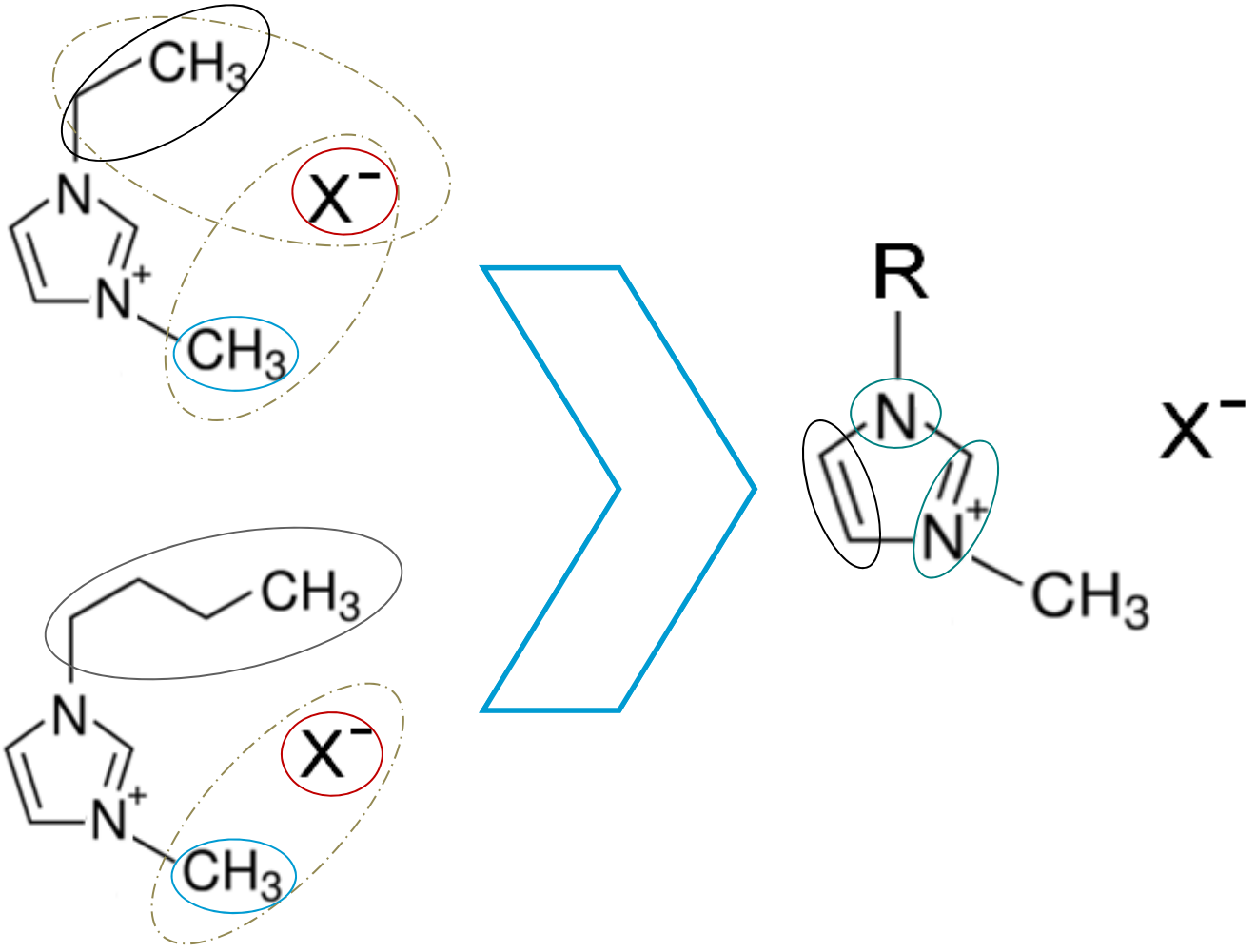
[EtMeIm]*X*

[BuMeIm]*X*



MECHANISM OF DECOMPOSITION

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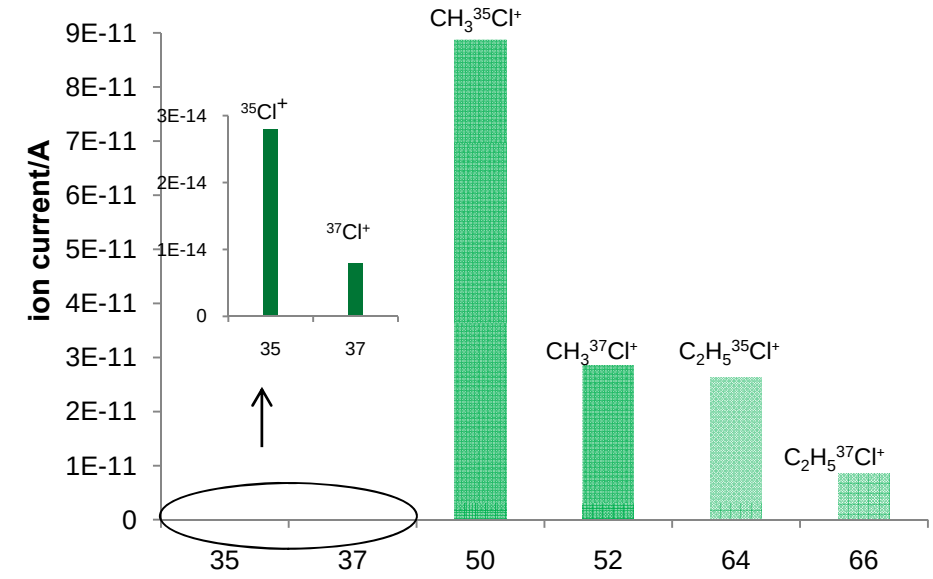
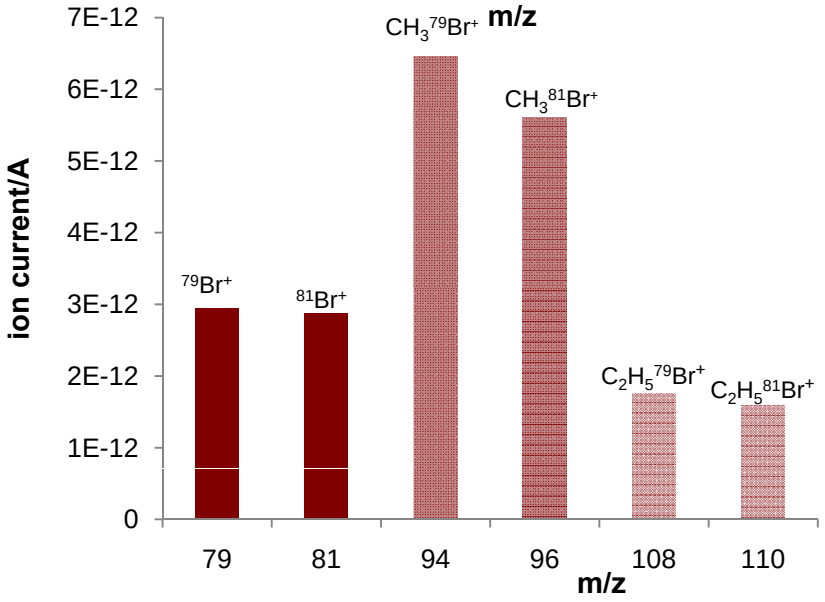
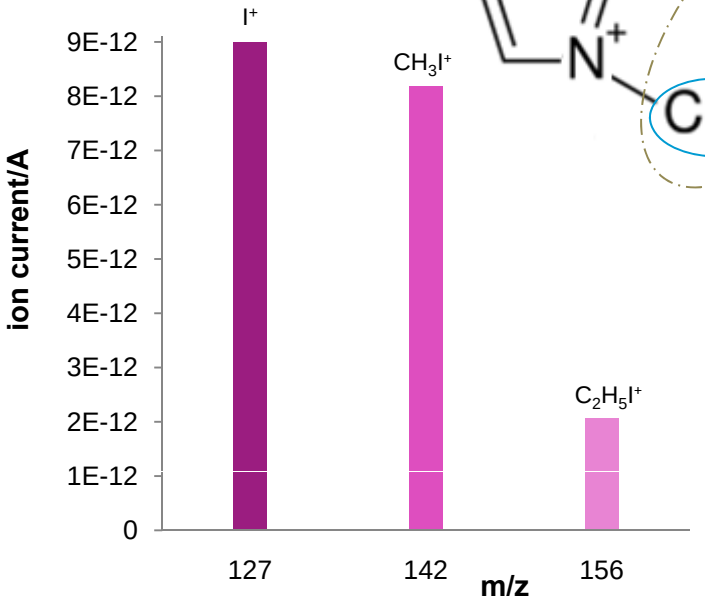


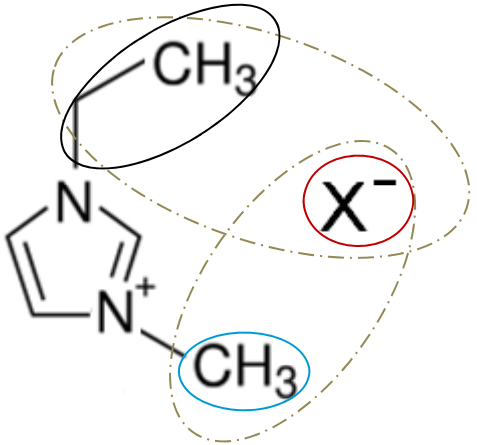




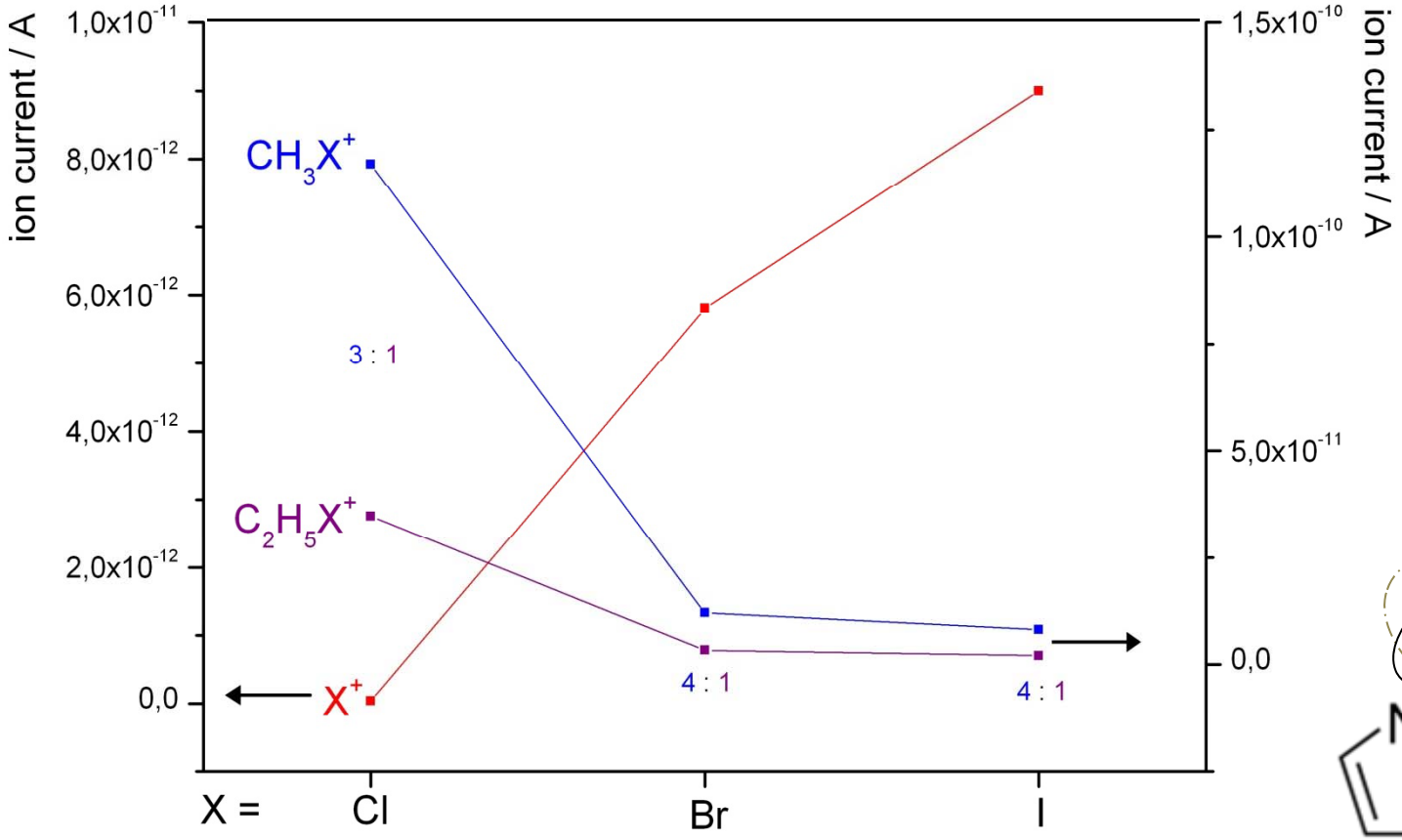
[EtMeIm] Cl : $CH_3Cl^+ > C_2H_5Cl^+ > Cl^+$

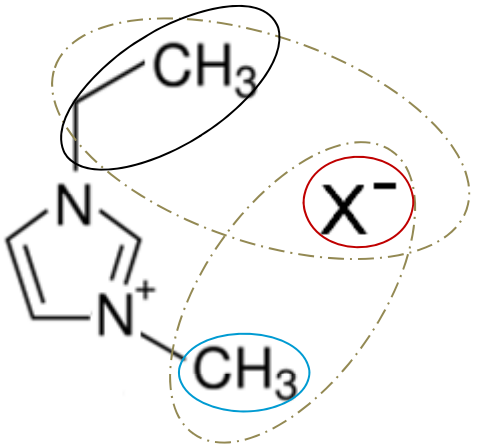
[EtMeIm] Br : $CH_3Br^+ > C_2H_5Br^+ \approx Br^+$

[EtMeIm] I : $CH_3I^+ \approx I^+ > C_2H_5I^+$



Mechanism of Decomposition





COCLUSIONS

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THERMAL PROPERTIES OF [RR´IM]X

-Supercooling and glass formation

- Formation of eutectic mixtures with low T_m and inhibition of crystallization

- Thermal stability up to 250 °C

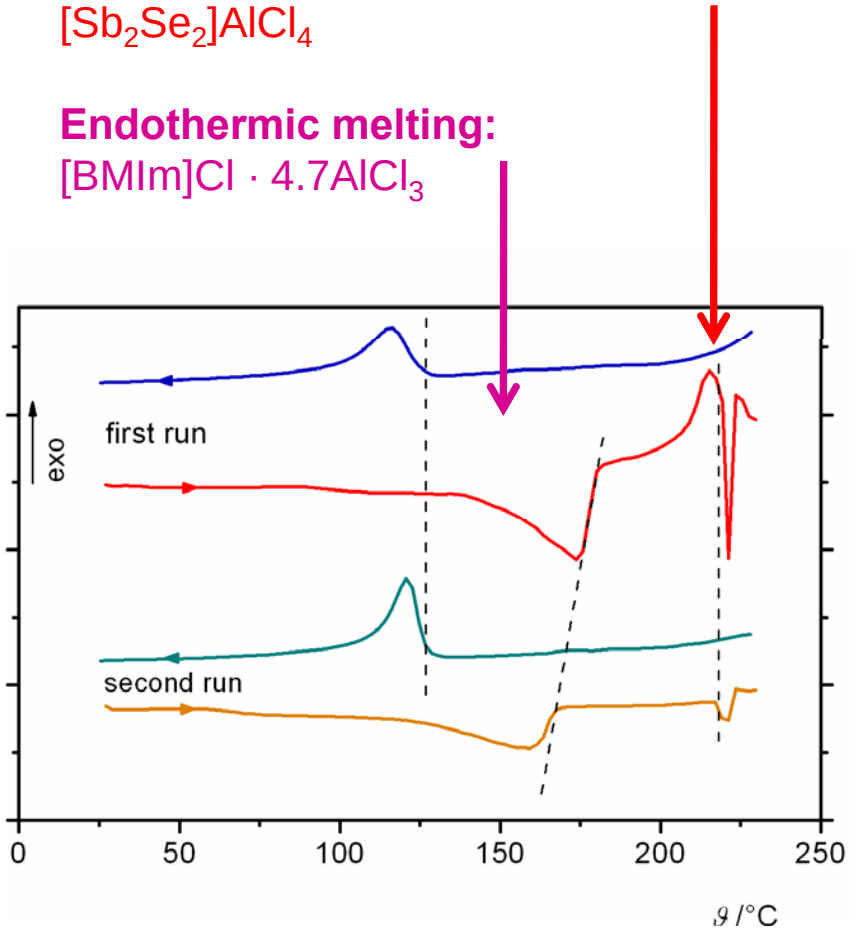
-Decomposition under formation of:

- -Alkylhalides
- -Alkanes
- -Ammonia

- Fragmentation pattern still unclear

Exothermic formation reaction:
$[Sb_2Se_2]AlCl_4$

Endothermic melting:
$[BMIm]Cl \cdot 4.7AlCl_3$



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DFG Deutsche Forschungsgemeinschaft

DFG - Priority Program:
Material Synthesis near Room Temperature

EFRE

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