

## Enhancing Task Specific Ionic Liquids' Thermal Stability by Structural Modification

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**Summary.** Thermal *retro-Michael* decomposition of task specific ionic liquids (TSILs) was efficiently suppressed by hydrogenation of the oxobutyl side chain yielding a hydroxy-functionalized TSIL.

**Keywords.** Ionic liquids; Thermal stability.

### Introduction

In recent years, functionalized ionic liquids have attracted much interest as task-specific ionic liquids (TSILs) [1]. One common approach for the synthesis of TSIL is to incorporate a functional group in the side chain of a pyridinium or imidazolium cation. This sort of TSIL finds application in the fields of catalysis [2] including biocatalysis [3], organic synthesis [4], extraction [5], dissolution [6], materials preparation [7], and electrochemistry [8]. One synthesis approach towards such ionic liquids is a *Michael*-type addition of a protonated ammonium salt to an  $\alpha,\beta$ -unsaturated carbonyl compound **1** yielding an oxobutyl functionalized cation **2** (Scheme 1) [9].

One potential drawback of this type of keto-functionalized ionic liquids is the reduced thermal stability due to the possibility for a *retro-Michael* reaction, leading to the loss of the functionalized side chain (Scheme 2).

One possible strategy to overcome this limitation is to convert the keto-functionalized IL in a consecutive reaction, such as *e.g.* hydrogenation, amination, *Wittig* reaction, *etc.*, thus eliminating the chance for the *retro-Michael* decomposition pathway. By this further functionalization numerous new functionalized TSIL may be available in a straight forward, two-step synthesis.

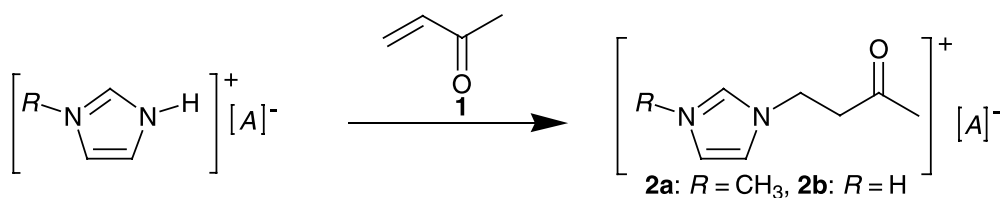
In this contribution we present in detail the stabilization of keto-functionalized cations by a heterogeneous catalyzed hydrogenation reaction yielding hydroxy-functionalized TSILs (Scheme 3).

### Results and Discussion

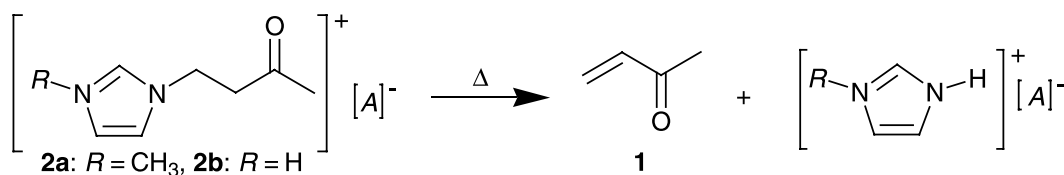
As starting materials, two *Michael*-type ionic liquids based on the 3-oxobutylimidazolium-cation were selected. Due to its well-known high thermal stability [10] the anion bis(trifluoromethanesulfonyl)imide ( $[NTf_2]^-$ ) was combined with these cations for our experiments. The hydrogenation of the oxobutyl functionalized cations in the presence of chiral anions has been already reported by us in an earlier contribution [11]. In this study, we focus on the thermal stability of the hydroxyl-functionalized ionic liquids **3** compared to the oxobutyl functionalized TSILs **2**.

All hydrogenation reactions were performed at 60°C and 60 bar H<sub>2</sub> according to Ref. [11] and full conversion was reached after 12 h with excellent selectivities of >99.5% (Scheme 3).

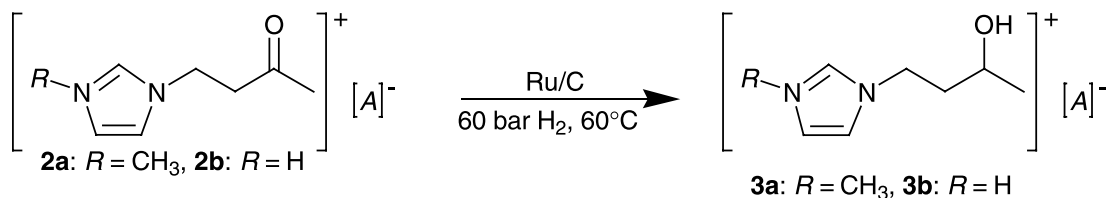
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Scheme 1



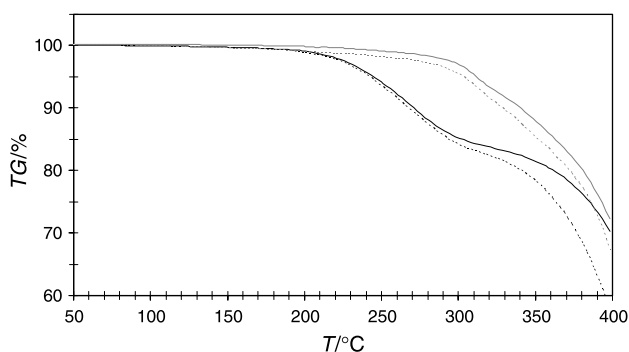
Scheme 2



Scheme 3

To confirm the stabilizing effect of the hydrogenated TSILs the thermal stabilities before and after the hydrogenation were determined by TGA measurements (Netzsch TG 209) using ramped experiments with a heating rate of 10 K/min under argon (Fig. 1).

As expected, the hydrogenated ionic liquids **3a** and **3b** showed a significant increase in thermal



**Fig. 1.** Thermal gravimetric analysis (TGA) of **2** and **3**. —: **2a**, ...: **2b**, —: **3a**, ...: **3b**

stability over the non-hydrogenated (**2a**, **2b**) ones. While the on-set temperature of the decomposition of the keto-functionalized ionic liquids is approx. 200°C, decomposition of the hydrogenated ionic liquids is not observed in the same experiment below 280°C.

The TGA measurements of **2a** and **2b** show a distinct mass-loss of approximate 15%, starting at 190°C. This observation was attributed to a first decomposition step which fits in its expected mass loss due – 16.3 and 16.8% for **2a** and **2b**, – very well to the assumption of a dealkylation by the *retro-Michael* reaction according to Scheme 2. To confirm this hypothesis further, a sample of **2a** was heated under vacuum to 220°C for 30 min and the decomposition products were collected in a cold trap. Subsequent analysis of the collected substance by NMR and GC/MS revealed that indeed pure methyl vinyl ketone **1** was collected as volatile decomposition product.

For most of the possible applications of TSIL, degradation rates between 100 and 200°C are of particular practical importance. Therefore, we decided

**Table 1.** Isothermal mass loss of **2** and **3** at 160°C

Ionic liquid	Mass loss/%mass h <sup>-1</sup> isothermal experiment
<b>2a</b>	0.40
<b>2b</b>	0.33
<b>3a</b>	0.08
<b>3b</b>	0.10

to study the decomposition of the TSILs **2a**, **2b** and **3a**, **3b** in more detail in this temperature range. In previous studies we and other groups had found that the decomposition rates of non-functionalized 1,3-dialkylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquids follow zero order decomposition kinetics over a wide decomposition range with no discernable differences in the decomposition mechanism [12]. Surprisingly, with the keto-functionalized ionic liquids **2a** and **2b** several decomposition regimes can be clearly distinguished.

The thermal stability of **2a**, **2b** and **3a**, **3b** was also determined below their on-set decomposition temperature (10 K/min) by isothermal stability experiments at 160°C over 12 h in argon atmosphere. Table 1 shows the respective mass losses of the ionic liquids per hour.

These results impressively confirm the higher thermal stability of the hydrogenated species **3a** and **3b** in comparison to **2a** and **2b** due to the suppression of the *retro-Michael* decomposition pathway.

Comparing the relative stabilities of **2a** vs. **2b** and **3a** vs. **3b** reveals a slightly lower stability of the protonated species.

It can be stated that within the accuracy of measurements, the stability of the ionic liquids at 160°C decreases in the order **3a** ≈ **3b** ≫ **2b** ≈ **2a**.

## Conclusion

In summary, we presented a new approach to thermally quite stable task-specific ionic liquids. While oxybutyl functionalized ionic liquids have been shown to be susceptible for decomposition by a *retro-Michael* pathway the thermal stability of these TSILs can be increased drastically by hydrogenation of the keto-bearing side chain giving access to ionic liquids with sec-alcohol functionalities in the cation.

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