Continuous-flow Synthesis of N,N'-Dimethylimidazolium-2-carboxylate – A Precursor for Halide-free Ionic Liquids

D. Habermann[1,*], D. Breuch[1] and H. Löwe[1,2,*]

[1] Johannes Gutenberg-University Mainz, Duesbergweg 10-14, 55128 Mainz
[2] Fraunhofer ICT-IMM, Carl-Zeiss-Str. 18-20, 55129 Mainz, Germany

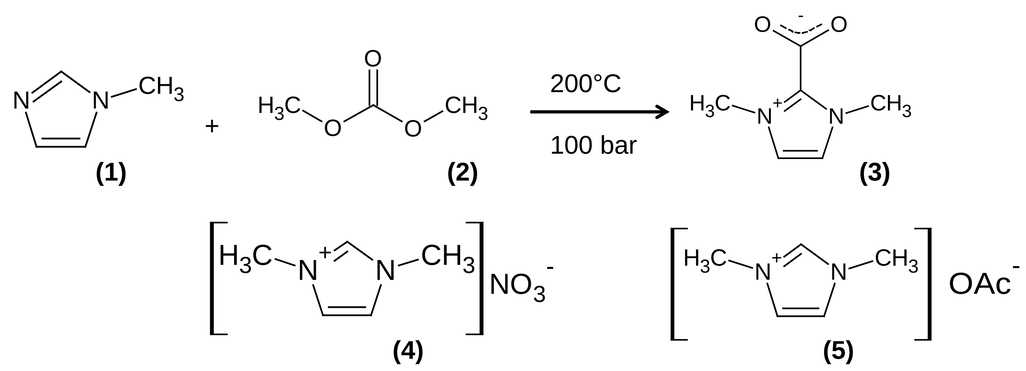
[*] habermann@uni-mainz.de, loewe@uni-mainz.de

Introduction

The synthesis of ionic liquids (ILs) is described in numerous books and publications with homogenous or heterogeneous catalysts, in many cases, at high temperatures, high pressure and long processing times up to days.[1] Because of the very low vapor pressure of ILs, it is not possible to purify them by distillation. That is why IL syntheses were performed with equimolar reactant ratios in micro-structured reactors under continuous flow conditions.[2] Besides these processing difficulties, the direct synthesis of ILs with unusual anions is not possible and a multi-step synthesis, based on anion exchange from ILs with halide anions is necessary.[3,4]

Since a couple of years the alkylation reaction of N-methylimidazole (MIM) **(1)** with dimethyl carbonate (DMC) **(2)** is under investigation (Scheme 1).[5-7] DMC is known as a clean and eco-friendly methylating agent which could be used as safe replacement of current reagents such as methylhalides, dimethyl sulfate and phosgene.[8] The Alkylation of **(1)** with **(2)** gives the respective solid zwitterion N,N`-dimethylimidazolium-2-carboxylate **(3)**, a versatile precursors for manufacturing of non-halide containing ILs.

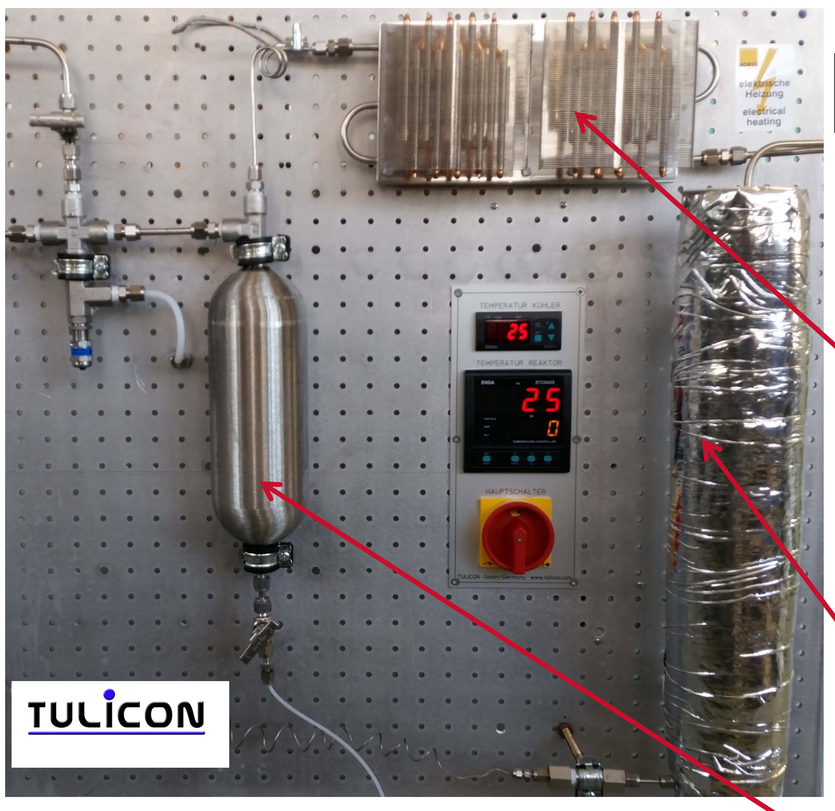
Reaction



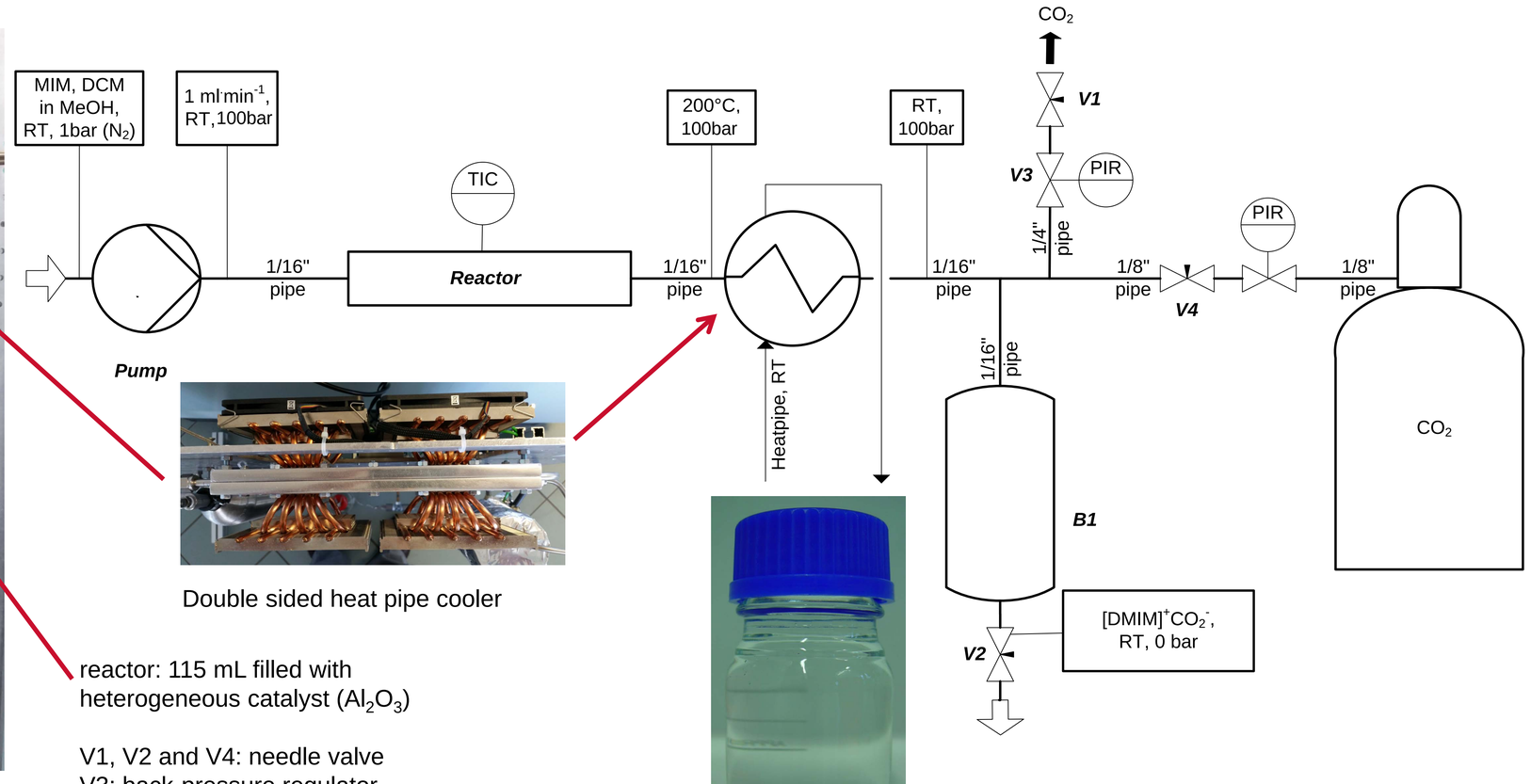
Experimental

MIM **(1)** and DMC **(2)** were premixed with methanol to avoid precipitations inside the tube reactor because of the formation of a non–soluble solid product **(3)**. The reactor, a 115 mL stainless steel tube, was filled with a heterogeneous catalyst (Al_2O_3) which reduces the free reactor volume down to 84 mL. A HPLC pump was used to apply a continuous and nearly pulsation-free flow a mixture of 1mol **(1),** 1.3mol **(2)** 210mL methanol (overall 400mL) with a flow rate of 20 mL min^{-1} (optimized conditions) into the electrically heated tube reactor (200°C). Cooling the reaction mixture to ambient is performed by a double sided heat-pipe array. Needle valves and a back-pressure regulator allow managing the reaction under pressure up to 100 bar. The complete decomposition of (2) release enough CO_2 to ensure a pressure self-regulation. The CO_2 compressed gas cylinder is only used for the start-up procedure and not necessary for pressure regulation while the process runs. A subsequent distillation allows to remove the excess of methanol and non-converted **(1)**. The carboxylate product **(3)** appears as a white crystalline powder and can be used for further conversion, e.g. to dimethylimidazolium nitrates **(4)** or –acetates **(5)**.

Flow-Scheme and Experimental Setup



(with permission from TULICON GmbH, Mainz, Germany)



Double sided heat pipe cooler

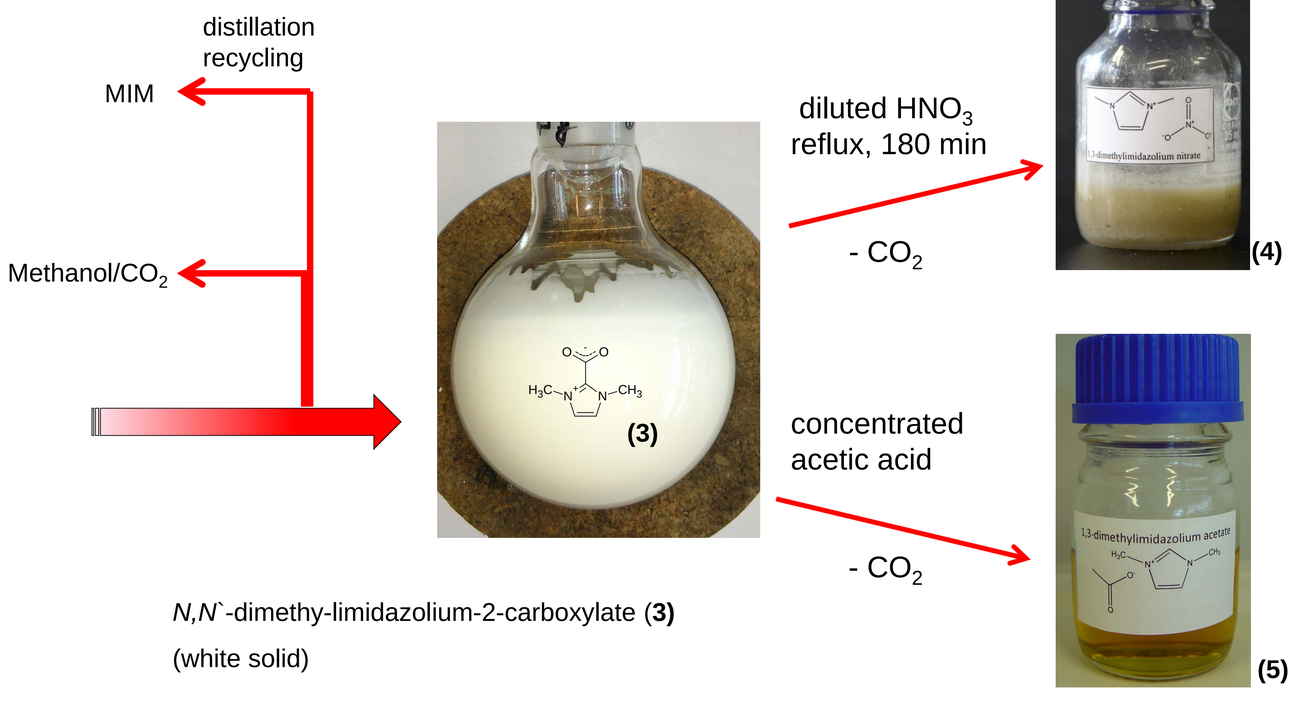
reactor: 115 mL filled with heterogeneous catalyst (Al_2O_3)

V1, V2 and V4: needle valve
V3: back-pressure regulator

B1: sample cylinder

nearly colourless reaction mixture

Results



N,N`-dimethy-limidazolium-2-carboxylate (**3**)

(white solid)

- Approx. 98% (HPLC) yield could be achieved:

temperature:	200°C
pressure	100 bar
flow rate:	20 mL min^{-1}
residence time:	2550 s (4.25 min)
yield:	~ 370 g h^{-1}

- Sustainable cooling by heat pipes
- No purification by repeatedly precipitation from ethyl acetate necessary
- Carbon dioxide and methanol will be the only side products. Both can be reused as DMC precursor
- Unreacted MIM **(1)** remains in the solvent and can be reused after purification. Heterogeneous catalyst enhances the reaction speed and yield significantly.
- The carboxylate **(3)** is a precursor for the synthesis numerous ILs by decarboxylation and anion introduction, e.g.

NO_3^-	titration of **(3)** with diluted HNO_3 under reflux
acetate	adding glacial acetic acid, heating up for several hours and purification by short path vacuum distillation

References

[1] J. S. Wilkes, P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2008**.
[2] T. Schäfer, C. M. Rodrigues, C. A. M. Afonso, J. G. Crespo, *Chem. Comm.*, **2001**, 1622
[3] E. Alcalde, I. Dinares, A. Ibanez, N. Mesquida, *Chem. Comm.,47 ,* **2011**, 3266
[4] I. Dinares, C. G. de Miguel, A. Ibanez, N. Mesquida, E. Alcalde, *Green Chem., 11,* **2009,** *1*507
[5] M. Lissel, *Ann. Chem.*, **1987**, 77
[6] M. Smiglak, et al., Gr*een Chem.*, 9, **2007**, *9*0
[7] N. J. Bridges, C. C. Hines, M. Smiglak, R. D. Rogers, *Chem. Eur. J.*, 13, **2007**, 5207
[8] P. Tundo, M. Selva, *Acc. Chem. Res.*, **2002**, *35* 706.

Acknowledgment

We acknowledge financial support by an AiF grant (KF3062501) funded by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. and for the establishing of special equipment from the TULICON GmbH, Mainz