Binary Alkoxide Ionic Liquids

McNeice, P., Marr, A. C., Marr, P. C., Earle, M. J., & Seddon, K. R. (2018). Binary Alkoxide Ionic Liquids. *ACS Sustainable Chemistry & Engineering*, 6(11), 13676–13680. <https://doi.org/10.1021/acssuschemeng.8b04299>

Published in:
ACS Sustainable Chemistry & Engineering

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

© 2018 American Chemical Society. This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Binary Alkoxide Ionic Liquids

Peter McNeice, Andrew C. Marr,* Patricia C. Marr,* Martyn J. Earle and Kenneth R. Seddon.†

Queen's University Ionic Liquids Laboratories and The School of Chemistry and Chemical Engineering, The Queen's University of Belfast, The David Keir Building, Stranmillis Road, Belfast, BT9 5AG, United Kingdom.

*Email: a.marr@qub.ac.uk (A.C.M.), p.marr@qub.ac.uk (P.C.M.).

Synopsis

We present new ionic liquid bases, which have low flammability and can potentially be recovered. They could replace traditional flammable, harmful bases, which are not recovered.

Abstract

Strongly basic, stable ionic liquids are rare. We report the synthesis of a series of stable binary alkoxide ionic liquids. The Hammett Basicity of these ionic liquids is comparable to or greater than traditional bases such as pyridine and NaOMe. The ionic liquids catalyse the Knoevenagel condensation of malononitrile and benzaldehyde, with the best system displaying higher activity than pyridine and NaOMe; and the Aldol condensation of acetone and benzaldehyde.

Keywords: Basic ionic liquids, Binary ionic liquids, Base catalysis, Knoevenagel condensation, Aldol condensation.

Introduction

Ionic liquids have many favourable properties such as low flammability and negligible vapour pressure, leading to them being hailed as green solvents.¹ The imidazolium cation, an extremely common cation reported for the preparation of ionic liquids, is very sensitive to bases, due to the presence of an activated (acidic) C-H between the nitrogen atoms of the ring.² Side reactions of this type are a major limitation to the application of basic ionic liquids and must be avoided as the first priority in ionic liquid design. A comprehensive review of the chemical stability of ionic liquids is available.³ Basic ionic liquids can be prepared by locating the basicity on the anion or cation. Anions can confer strong basicity, but often lead to instability as the anion can attack the cation, causing breakdown of the ionic liquid.⁴ This limits the use of the ionic liquid as it will prevent successful recycle. Basicity can alternately be located on the cation, usually on free Lewis basic sites. Basic ionic liquids designed in this way tend to be more stable,⁵ but often experience low basicity due to withdrawal of electron density from the Lewis base by the cation.^{6,7} Stable, strongly basic ionic liquids are scarcely known. Here we report a class of binary alkoxide ionic liquids with strong basicity.

The traditional instability of basic ionic liquids has been solved here by developing a new class of binary ionic liquids; [Pyrr₁₄][NTf₂]_x[OⁱPr]_{1-x}. Binary ionic liquids contain more than two ions and provide the potential to synthesise 10¹⁸ ionic liquids,⁸ as each combination of cations and anions produces an ionic liquid with unique properties. Binary ionic liquids have found use in combining the favourable properties of two ionic liquids in order to perform a particular function. They have been applied to the one-pot dissolution and dehydration of cellulose to form a mixture of products, in this way 100 % cellulose conversion has been achieved.⁹ Despite the promise of acidic binary ionic liquids, binary mixtures containing Brønsted basic ionic liquids are few.^{10,11} This work communicates a binary ionic liquid comprising a small amount of basic ionic liquid mixed with a neutral, water immiscible ionic liquid. The basic ionic liquid provides the desired basicity, whilst the neutral ionic liquid allows a room temperature mixture to form. The addition of the third ion ([NTf₂]⁻) is observed

to stabilise the basic species. This may occur through a combination of coulombic interactions and the adoption of the properties of the dopant, as a hydrophobic ionic liquid will experience much lower rates of hydrolytic decomposition. Intermolecular forces such as hydrogen bonding, π - π stacking and van der Waals' forces are thought to contribute less to the stability as they are known to be less effective when more than two ions are present.¹² The synthesis of $[\text{Pyrr}_{14}][\text{NTf}_2]_x[\text{O}^i\text{Pr}]_{1-x}$ ionic liquids is straightforward, and they are simply applied to base catalysed reactions, as outlined below.

Results and Discussion

1-butyl-1-methyl pyrrolidinium ($[\text{Pyrr}_{14}]^+$) was selected as the cation for binary basic alkoxide ionic liquids as cyclic ammonium cations are known to be relatively base stable¹³ and have the added advantage of being less toxic than imidazolium derived cations.¹⁴ Sodium *iso*-propoxide (NaO^iPr) was prepared by refluxing sodium metal dissolved in *i*-PrOH. The cooled mixture was added to $[\text{Pyrr}_{14}][\text{Br}]$, upon which NaBr precipitated, driving the formation of $[\text{Pyrr}_{14}][\text{O}^i\text{Pr}]$, which we have found to be relatively stable in solution. The $[\text{Pyrr}_{14}][\text{O}^i\text{Pr}]$ solution was added in small quantities to varying amounts of neutral $[\text{Pyrr}_{14}][\text{NTf}_2]$, to yield binary ionic liquids with different ratios of ions. Upon removal of the solvent *in vacuo*, basic, room-temperature ionic liquids of general formula $[\text{Pyrr}_{14}][\text{NTf}_2]_x[\text{O}^i\text{Pr}]_{1-x}$ were produced. The initial ^1H NMR spectra showed no degradation of the cation, resonances due to $[\text{O}^i\text{Pr}]^-$ are clearly visible (NMR Spectra are in the ESI S3.1.1-S6.6.2). The stability is likely to arise from a combination of factors. An important variable is the relatively low proportion of basic species in the system, which will limit attack of the basic anion on the cation. As the diffusion of ions is relatively slow in ionic liquids, this is likely to contribute a marked improvement in stability. The basic anion will interact strongly with the other ions due to ionic/coulombic interactions, the dominant interaction in ionic liquids, and this will inhibit its mobility and reduce its propensity to nucleophilically attack a specific point of reactivity on the cation. Reduced mobility has been proposed to reduce the basicity of hydroxide ion¹⁵ and metal alkoxides.¹⁶ The effect is also seen in aqueous systems where water interacts with hydroxide ions to form a hydration sphere, increasing the stability of anion exchange membranes to a greater extent than would be expected solely due to reduced concentration of hydroxide ions.¹⁵ The mobility of ions within the ionic liquid will be related to the viscosity.

Determination of the pH of an ionic liquid is not possible when it is insoluble or unstable in water. The Hammett function (H_0) has been used to give a measurement of the acidity of non-aqueous Brønsted acid systems,¹⁷ and has more recently been used to determine basicity in non-aqueous systems.^{18,19} The Hammett basicity (H_-) of the binary ionic liquids was measured by monitoring the UV absorbance of methanolic bromocresol green at a fixed concentration of ionic liquid. The basicity is not reliant on $[\text{Pyrr}_{14}][\text{NTf}_2]$ or residual $[\text{Pyrr}_{14}][\text{Br}]$ as these ionic liquids are unable to deprotonate the indicator molecule. The ionic liquids $[\text{Pyrr}_{14}][\text{NTf}_2]_x[\text{O}^i\text{Pr}]_{1-x}$ displayed basicity greater than several traditional bases, and comparable to NaOMe (Table 1). The Hammett basicity of the binary ionic liquids measured was not found to increase systematically with increased mole fraction of the basic anion (Table 1, entries 1-4). This may be because interactions between the basic anion and the other ions are reducing the basicity. Upon mixing two ionic liquids the interionic interactions often do not change linearly^{12,20}

Table 1: Hammett basicity of ionic liquids and traditional bases.

Entry	Base	Hammett Basicity ^a ($\pm$, SD)	$T_{\text{degradation}}$ ($^{\circ}\text{C}$) ^b
1	$[\text{Pyrr}_{14}][\text{NTf}_2]_{0.95}[\text{O}^i\text{Pr}]_{0.05}$	10.43 (0.019)	233
2	$[\text{Pyrr}_{14}][\text{NTf}_2]_{0.85}[\text{O}^i\text{Pr}]_{0.15}$	10.40 (0.009)	242

3	[Pyrr ₁₄][NTf ₂] _{0.68} [O ⁱ Pr] _{0.32}	10.44 (0.008)	242
4	[Pyrr ₁₄][NTf ₂] _{0.58} [O ⁱ Pr] _{0.42}	10.40 (0.021)	230
5	Pyridine	7.88 (0.097)	-
6	Et ₃ N	10.36 (0.027)	-
7	DBU	10.42 (0.021)	-
8	KOH	10.46 (0.009)	-
9	NaOMe	10.51 (0.027)	-

^a Determined by monitoring UV absorbance at 619 nm of a 0.09 mM solution of IL in bromocresol green, value is an average of three samples. ^b Degradation onset temperature measured by thermogravimetric analysis.

Measurement of ¹H and ¹⁹F NMR spectra for 8 months and the Hammett basicity over 14 weeks (Figure 1, ESI Table S2) showed no significant differences. These results suggest that the ionic liquids are stable under ambient conditions. The decomposition mechanisms of the pyrrolidinium cation are well known;¹³ ring opening *via* nucleophilic substitution or β-hydride elimination, methyl substitution and β-hydride elimination on the butyl chain. These mechanisms can be followed by ¹H NMR. A signal emerging at ~0.8 ppm would indicate ring opening, disappearance of the methyl signal at ~3.0 ppm would indicate methyl substitution, and changes in the butyl integration could indicate β-hydride elimination. The ¹H NMR spectra of [Pyrr₁₄][NTf₂]_x[OⁱPr]_{1-x} ionic liquids remained consistent, and no decomposition was evident. The ¹⁹F NMR spectra of [Pyrr₁₄][NTf₂]_x[OⁱPr]_{1-x} ionic liquids remained a single resonance indicating that the [NTf₂]⁻ anion is stable in this class of ionic liquids. If the basic anion attacked the cation, entirely consuming the anion, the Hammett basicity would decrease. There would be no basic species left in solution to deprotonate the indicator. For all ionic liquids the Hammett value fluctuated, but remained reproducible (within reasonable error limits), so by this method the ionic liquids appear to be stable (ESI Table S2). The ionic liquids were kept relatively dry by periodic drying under vacuum. The Hammett values tend to decrease and stabilise after drying. Ionic liquids are expected to absorb water from the atmosphere. Wetting would make the ionic liquids less viscous, increasing the mobility of the basic anions and allowing them to better deprotonate the indicator. Wetting is also expected to lead to the formation of hydroxide ions due to the equilibrium between water - isopropoxide and hydroxide - isopropanol.

Figure 1: ¹H NMR spectra of [Pyrr₁₄][NTf₂]_{0.85}[OⁱPr]_{0.15}. Bottom to top: initial, 4 days, 2 weeks, 8 months.

Thermal stability as assessed by thermogravimetric analysis (TGA, ESI section 8) showed that the $[\text{Pyrr}_{14}][\text{NTf}_2]_x[\text{O}^i\text{Pr}]_{1-x}$ ionic liquids have similar thermal stability regardless of the ratio of the basic component with no clear systematic variance (Table 1, entries 1-4). This agrees with studies on $[\text{EMIM}][\text{EtSO}_4]_x[\text{NTf}_2]_{1-x}$ which show reasonably constant thermal stability regardless of the proportion of nucleophilic $[\text{EtSO}_4]$.²¹

Knoevenagel condensation was introduced as a test reaction for base catalysed reactions in ionic liquids by Davis and co-workers.²² The basicity of the ionic liquids was demonstrated by their ability to act as catalysts for the Knoevenagel condensation of malononitrile and benzaldehyde (Figure 2). Control experiments showed that $[\text{Pyrr}_{14}][\text{NTf}_2]$ is unable to catalyse the reaction (Table 2, entry 1). As the proportion of basic anion in the ionic liquid increases, but the total amount of ionic liquid is kept constant, the reaction yield increases. This shows that the reaction is sensitive to the basic catalyst loading under these conditions. The best result obtained was 89% (for $[\text{Pyrr}_{14}][\text{NTf}_2]_{0.58}[\text{O}^i\text{Pr}]_{0.42}$). Keithellakpam *et al.*²³ used a basic cation based on hexamethylenetriamine (HMTA) in water to catalyse the same reaction. The isolated yields in Keithellakpam's system ranged from 82 % to 100 %. The catalyst loading was 5-30 mole % (compared to 1 mole % ionic liquid concentration in this work). Forsythe *et al.*⁶ used a series of ionic liquids with a Hunig's Base motif appended to an ammonium cation in the neat Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. The reaction time varied from twenty minutes to one hour and the conversion of benzaldehyde ranged from 12 % to 91 %. While the ethyl cyanoacetate is less active than malononitrile, 10 mole % of the ionic liquids was used. Thus, this work provides comparable catalytic results in the Knoevenagel reaction to previous ionic liquid systems at lower base concentration.

Figure 2: Knoevenagel condensation between benzaldehyde and malononitrile.

Table 2: Contained yield of Knoevenagel condensation catalysed by 1 mole % basic catalyst.

Entry	Basic Catalyst	Contained Yield ^a
1	$[\text{Pyrr}_{14}][\text{NTf}_2]$	0
2	$[\text{Pyrr}_{14}][\text{NTf}_2]_{0.95}[\text{O}^i\text{Pr}]_{0.05}$	24
3	$[\text{Pyrr}_{14}][\text{NTf}_2]_{0.85}[\text{O}^i\text{Pr}]_{0.15}$	32
4	$[\text{Pyrr}_{14}][\text{NTf}_2]_{0.68}[\text{O}^i\text{Pr}]_{0.32}$	81
5	$[\text{Pyrr}_{14}][\text{NTf}_2]_{0.58}[\text{O}^i\text{Pr}]_{0.42}$	89
6	Pyridine	89
7	NaOMe	79

Conditions: Malononitrile (0.087 g, 1.32 mmol), benzaldehyde (0.15 g, 1.41 mmol), basic catalyst (1 mole %) (RT, stir rate 500 RPM and time 1 h). ^aObtained from ¹H NMR against a known mass of ethyl trifluoroacetate.

It is interesting to note that the most effective binary basic ionic liquid catalysts (

Table 2, entries 4, 5) produce a similar yield to the traditional bases pyridine and sodium methoxide (

Table 2, entries 6, 7). This is despite the fact that only 1 mole % of catalyst was used in each reaction, and the basic species present in the ionic liquid experiments is at a concentration considerably less than 1 mole %. Theoretical calculations have shown that the elimination of hydroxide to form the final product is the rate limiting step in a similar Knoevenagel condensation in methanol.²⁴ The polar nature of the ionic liquid would favour this elimination. The reaction proves that [Pyrr₁₄][NTf₂]_x[OⁱPr]_{1-x} ionic liquids can act catalytically. For example, [Pyrr₁₄][NTf₂]_{0.68}[OⁱPr]_{0.32} can produce a yield of 81 % (

Table 2, entry 4) despite the catalyst only providing 0.32 mole % of basic catalyst.

The binary alkoxide ionic liquids were applied to the Aldol condensation between benzaldehyde and acetone to produce hydroxy ketone **1** and α,β -unsaturated ketone **2** (Figure 3). This demonstrates that these binary ionic liquids can catalyse a less activated system. Homogeneous Aldol reactions are performed industrially by alkaline bases.^{25,26} These systems suffer loss of base due to separation problems, corrosion of reactors, and the production of waste salts which need to be disposed of. Sulfolane was chosen as a co-solvent in order to suppress precipitation and side-reactions by diluting the catalyst and reagents. Sulfolane is a high boiling point solvent that is easily handled and recovered in industry whilst also being resistant to acids and bases,²⁷ it is also an “environmentally recommended” solvent.²⁸ One equivalent of [Pyrr₁₄][NTf₂]_{0.57}[OⁱPr]_{0.43} was used with sulfolane as a co-solvent. The reaction was found to be solvent dependent and initial yields obtained were low, (ca. 29 %). Optimisation of the reaction led to a marked improvement (Table 3). An average yield of 75 % was achieved for [Pyrr₁₄][NTf₂]_{0.57}[OⁱPr]_{0.43} (Table 3, entry 1). As with the Knoevenagel condensation, when a lower proportion of basic anion is present the yield decreased (Table 3, entries 2, 3).

Figure 3: Aldol condensation between benzaldehyde and acetone.

Table 3: Crude yield of Aldol condensation catalysed by 1 equivalent of basic catalyst

Entry	Catalyst	Crude Yield (1%/2%) ^a
1	[Pyrr ₁₄][NTf ₂] _{0.57} [O ⁱ Pr] _{0.43}	75 (15/60)
2	[Pyrr ₁₄][NTf ₂] _{0.67} [O ⁱ Pr] _{0.33}	28 (22/6)
3	[Pyrr ₁₄][NTf ₂] _{0.84} [O ⁱ Pr] _{0.16}	12 (8/4)
4	NaOH ^b	69 (0/69)

Conditions: Benzaldehyde (0.023 g, 0.22 mmol, 1 eq.), acetone (0.228 g, 3.93 mmol, 10 eq.), [Pyrr₁₄][NTf₂]_x[OⁱPr]_{1-x} (0.083 g, 0.20 mmol 1 eq.), sulfolane (0.501 g, 4.17 mmol, 1 mL/0.5 mmol IL), (25 °C, 1.5 hours, stir rate 500 RPM). ^a Obtained from ¹H NMR of extracted organics against a known mass of ethyl trifluoroacetate. ^b 1 eq 2M aqueous NaOH, no sulfolane.

When aqueous NaOH was used as a catalyst only **2** was formed (Table 3, entry 4). The basic alkoxide ionic liquids yielded both **1** and **2**, with **2** dominant for the most basic systems. Dehydration is the rate limiting step of traditional aldol reactions, which often do not go to completion when acetone is a reagent.²⁹ It has also been proposed that the dehydration step is reversible.³⁰

The same aldol reaction was previously reported as catalysed by 30 mole % guanidine acetate under solventless conditions, 92 % yield was obtained after 7 hours.³¹ An 88 % yield was obtained when 5 mole % of a [choline][proline] catalyst was used with water as solvent after 12 hours.³²

While the literature examples use less than 1 equivalent of basic ionic liquid, the loading of ionic liquid is frequently high. The low proportion of basic species in the binary alkoxide ionic liquid system should be safer as this should be less corrosive without being less effective. This, combined with the extremely low flammability and relatively low toxicity, suggests that binary basic ionic liquids of this class could provide highly active, safer alternatives to traditional bases.

Conclusions

A series of stable, strongly basic binary alkoxide ionic liquids have been prepared. These ionic liquids show high Hammett basicity and have been used to successfully catalyse both the Knoevenagel condensation of malononitrile and benzaldehyde and the Aldol condensation of acetone and benzaldehyde. The method used for synthesis involves adding small proportions of basic ionic liquids to base stable hydrophobic ionic liquids. The synthesis of these ionic liquids is versatile and provides the opportunity to create many more classes of basic ionic liquids by using different stable ionic liquids in combination with basic anions.

Supporting Information

Details of materials and methods, IL synthesis, Hammett basicity, Knoevenagel experimental details, Aldol experimental details, NMR, FTIR, TGA.

Funding Source

Queen's University Ionic Liquid Laboratories

Acknowledgements

The industrial advisory board of Queens University Ionic Liquid Laboratories and Queen's University Belfast, School of Chemistry and Chemical Engineering.

References

- ¹ Earle, M. J.; Seddon, K. R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.*, **2000**, 72, 1391-1398, DOI: 10.1351/pac200072071391.
- ² Olofson, R. A.; Thompson, W. R.; Michelman, J. S. Heterocyclic nitrogen ylides. *J. Am. Chem. Soc.*, **1964**, 86, 1865-1866, DOI: 10.1021/ja01063a051.
- ³ Wang, B.; Qin, L.; Mu, T.; Xue, Z.; Gao, G. Are Ionic Liquids Chemically Stable?, *Chem. Rev.*, **2017**, 117, 7113-7131, DOI: 10.1021/acs.chemrev.6b00594.
- ⁴ Yuen, A. K. I.; Masters, A. F.; Maschmeyer, T. 1,3-Disubstituted imidazolium hydroxides: Dry salts or wet carbenes?. *Catal. Today*, **2013**, 200, 9-16, DOI: 10.1016/j.cattod.2012.04.007.
- ⁵ MacFarlane, D. R.; Pringle, J. M.; Johansson, K. M.; Forsyth, S. A.; Forsyth, M. Lewis basic ionic liquids. *Chem. Commun.*, **2006**, 1905-1917, DOI: 10.1039/B516961P.

- ⁶ Forsyth, S. A.; Fröhlich, U.; Goodrich, P.; Gunaratne, H. Q. N.; Hardacre, C.; McKeown, A.; Seddon, K. R. Functionalised ionic liquids: Synthesis of ionic liquids with tethered basic groups and their use in Heck and Knoevenagel reactions. *New J. Chem.*, **2010**, 34, 723–731, DOI: 10.1039/B9NJ00729F.
- ⁷ Fröhlich, U. Chirality and ionic liquids. PhD Thesis, Queen's University Belfast, 2005.
- ⁸ Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.*, **2008**, 37, 123-150, DOI: 10.1039/B006677J.
- ⁹ Long, J.; Guo, B.; Li, X.; Jiang, Y.; Wang, F.; Tsang, S. C.; Wang, L.; Yu, K. One step catalytic conversion of cellulose to sustainable chemicals utilizing cooperative ionic liquid pairs. *Green Chem.*, **2011**, 13, 2334-2338, DOI: 10.1039/C1GC15597K.
- ¹⁰ Wang, B.; Elageed, E. H. M.; Zhang, D.; Yang, S.; Wu, S.; Zhang, G.; Gao, G. One-Pot Conversion of Carbon Dioxide, Ethylene Oxide, and Amines to 3-Aryl-2-oxazolidinones Catalyzed with Binary Ionic Liquids. *ChemCatChem*, **2014**, 6, 278-283, DOI:10.1002/cctc.201300801.
- ¹¹ Saita, S.; Kohno, Y.; Nakamura, N.; Ohno, H. Ionic liquids showing phase separation with water prepared by mixing hydrophilic and polar amino acid ionic liquids. *Chem. Commun.*, **2013**, 49, 8988-8990, DOI: 10.1039/C3CC45302B.
- ¹² Chatel, G.; Pereira, J. F. B.; Debbeti, V.; Wang, H.; Rogers, R. D. Mixing ionic liquids—"simple mixtures" or "double salts"? *Green Chem.* **2014**, 16, 2051-2083, DOI: 10.1039/C3GC41389F.
- ¹³ Marino, M. G.; Kreuer, K. D. Alkaline stability of quaternary ammonium cations for alkaline fuel cell membranes and ionic liquids. *ChemSusChem.*, **2015**, 8, 513-523, DOI: 10.1002/cssc.201403022.
- ¹⁴ Frade, R. F. M.; Rosatella, A. A.; Marques, C. S.; Branco, L. C.; Kulkarni, P. S.; Mateus, N. M. M.; Afonso, C. A. M.; Duarte, C. Toxicological evaluation on human colon carcinoma cell line (CaCo-2) of ionic liquids based on imidazolium, guanidinium, ammonium, phosphonium, pyridinium and pyrrolidinium cations. *Green Chem.*, **2009**, 11, 1660-1665, DOI: 10.1039/B914284N.
- ¹⁵ Tuckerman, M. E.; Marx, D.; Parrinello, M. The nature and transport mechanism of hydrated hydroxide ions in aqueous solution. *Nature*, **2002**, 417, 925-929, DOI:10.1038/nature00797.
- ¹⁶ Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P.; *Metal Alkoxides*, Academic Press, New York, 1978, ch. 3.
- ¹⁷ Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. Determination of an acidic scale in room temperature ionic liquids. *J. Am. Chem. Soc.*, **2003**, 125, 5264-5265, DOI: 10.1021/ja0297382.
- ¹⁸ Li, W.; Zhang, Z.; Han, B.; Hu, S.; Song, J.; Xie, Y.; Zhou, W. Switching the basicity of ionic liquids by CO₂. *Green Chem.*, **2008**, 10, 1142-1145, DOI: 10.1039/B811624E.
- ¹⁹ Rizzo, C.; D'Anna, F.; Noto, R. Functionalised diimidazolium salts: the anion effect on the catalytic ability. *RSC Adv.*, **2016**, 6, 58477-58484, DOI: 10.1039/C6RA12037G.
- ²⁰ Niedermeyer, H.; Hallett, J. P.; Villar-Garcia, I. J.; Hunt, P. A.; Welton, T. Mixtures of ionic liquids. *Chem. Soc. Rev.*, **2012**, 41, 7780-7802, DOI: 10.1039/C2CS35177C.
- ²¹ Pinto, A. M.; Rodríguez, H.; Colón, Y. J.; Acre, A. Jr.; Acre, A.; Soto, A. Absorption of Carbon Dioxide in Two Binary Mixtures of Ionic Liquids. *Ind. Eng. Chem. Res.*, **2013**, 52, 5975-5984, DOI: 10.1021/ie303238h.
- ²² Morrison, D. W.; Forbes, D. C.; Davis Jr, J. H. Base-promoted reactions in ionic liquid solvents. The Knoevenagel and Robinson annulation reactions. *Tetrahedron Lett.*, **2001**, 42, 6053-6055, DOI: 10.1016/S0040-4039(01)01228-X.
- ²³ Keithellakpam, S.; Moirangthem, N.; Laitonjam, W. S. A simple and efficient procedure for the Knoevenagel condensation catalyzed by [MeHMTA][BF₄] ionic liquid. *Indian J. Chem., Sect B*, **2015**, 54, 1157-1161.
- ²⁴ Dalessandro, E. V.; Collin, H. P.; Valle, M. S.; Pliego Jr. J. R. Mechanism and free energy profile of base-catalyzed Knoevenagel condensation reaction. *RSC Adv.*, **2016**, 6, 57803-57810, DOI: 10.1039/C6RA10393F.
- ²⁵ Gradeff, P. S.; Rhodia inc. Process for preparation of methyl ionones. U.S. Patent 3840601A, October 8, 1974.
- ²⁶ Mitchell, P. W. D. Preparation of pseudoionones. U.S. Patent 4,874,900, October 17, 1989.
- ²⁷ Tilstam, U. Sulfolane: a versatile dipolar aprotic solvent. *Org. Process Res. Dev.*, **2012**, 16, 1273-1278, DOI: 10.1021/op300108w.
- ²⁸ Prat, D.; Hayler, J.; Wells, A. A survey of solvent selection guides. *Green Chem.*, **2014**, 16, 4546-4551, DOI: 10.1039/C4GC01149J.
- ²⁹ Noyce, D. S.; Reed, W. L. Carbonyl Reactions. IX. The Rate and Mechanism of the Base-catalyzed Condensation of Benzaldehyde and Acetone. Factors Influencing the Structural Course of Condensation of Unsymmetrical Ketones. *J. Am. Chem. Soc.*, **1959**, 81, 624-628, DOI:10.1021/ja01512a030.
- ³⁰ Podrebarac, G. G.; Ng, F. T. T.; Rempel, G. L. A kinetic study of the aldol condensation of acetone using an anion exchange resin catalyst. *Chem. Eng. Sci.*, **1997**, 52, 2991-3002, DOI:10.1016/S0009-2509(97)00098-5.
- ³¹ Zhu, A.; Jiang, T.; Han, B.; Huang, J.; Zhang, J.; Ma, X. Study on guanidine-based task-specific ionic liquids as catalysts for direct aldol reactions without solvent. *New J. Chem.*, **2006**, 30, 736-740, DOI: 10.1039/B600277C.

³² Hu, S.; Jiang, T.; Zhang, Z.; Zhu, A.; Han, B.; Song, J.; Xie, Y.; Li, W. Functional ionic liquid from biorenewable materials: synthesis and application as a catalyst in direct aldol reactions. *Tetrahedron Lett.*, **2007**, 48, 5613-5617, DOI: 10.1016/j.tetlet.2007.06.051.

Abstract Graphic

Binary alkoxide ionic liquids of general formula $[\text{Pyrr}_{14}][\text{NTf}_2]_x[\text{O}^i\text{Pr}]_{1-x}$ were found to act as basic catalysts. They were shown to be effective in Knoevenagel and Aldol condensations. Stable basic ionic liquids are potential replacements for unstable, volatile and corrosive bases.