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Complete List of Authors:	Nowicki, Janusz; Institute of Heavy Organic Synthesis , Muszyński, Marcin; Institute of Heavy Organic Synthesis Mikkola, Jyri-Pekka; Umea University; Abo Akademi University
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Ionic Liquids Derived from Organosuperbases: *en route* to Superionic Liquids

Janusz Nowicki[a*], Marcin Muszyński[a], Jyri-Pekka Mikkola[b,c*]

[a]*Institute of Heavy Organic Synthesis "Blachownia", Energetyków 9, 47-225 Kędzierzyn-Koźle, Poland*

[b]*Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-90871, Umeå, Sweden*

[c]*Industrial Chemistry & Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500, Åbo-Turku, Finland*

[*]*Corresponding authors: e-mail: nowicki.j@icso.com.pl; Jyri-Pekka.Mikkola@chem.umu.se*

Abstract

Interest in ionic liquids with guanidine, amidine and other superbasic cations has intense grown markedly in recent years. The syntheses, characterization and properties both of protic or quaternary alkylated salts based on cyclic or acyclic guanidine and amidine derivatives have been described in detail. By modifying the anion or the cation, a wide range of properties of superbasic ionic liquids can be tuned, including viscosity, melting point, density, conductivity, solubility, liquid range, thermal and hydrolytic stability. They are promising solvents for electrochemical, photovoltaic and various synthetic applications, in particular as specific catalysts. Due of their specific properties supebasic ionic liquids can be used in selected field of application of great industrial importance, e.g. CO_2, SO_2 or COS chemisorption.

1 Introduction

In general, the term "superbase" is usually referring to a compound characterized by its extreme basicity, this being exhibited by a very high affinity for protons. From a general point of view, the strongest 'normal' base is a hydroxide ion in case of aqueous solutions. Nevertheless, some bases exist with much greater base strengths than can be found in water. Such bases, commonly known as "superbases", are very important from the viewpoint of broadly understood organic synthesis and are fundamental in studies involving physical organic chemistry. In fact, the existence of superbases has been well known already since 1850.[1] In laboratory practice, the handling of superbases often requires special techniques because of their sensitivity to water, atmospheric carbon dioxide as well as oxygen. Inert atmosphere techniques and low temperatures minimize any of the potential side reactions that might occur.

IUPAC defines superbases simply as "compounds having a very high basicity, such as lithium diisopropylamide”.[2] On the other hand, Caubère defines superbases more precisely: "The term superbases should only be applied to bases resulting from a mixing of two (or more) bases leading to new basic species possessing inherent new properties. The term “superbase” does not mean a base is thermodynamically and/or kinetically stronger than another, instead it means that a basic reagent is created by combining the characteristics of several different bases”.[3]

Organic superbases are almost always neutral, nitrogen-containing species. Despite their enormous proton affinity, organosuperbases are prized for their enhanced reactivity which can be tempered by low nucleophilicity and good reactivity at relatively mild conditions. From the organic synthesis point of view, increasingly important superbases can be found in the families of phosphazene, amidine and guanidine derivatives. Still, many other organic compounds also meet the physicochemical or structural definitions justifying the classification term superbase.[4]

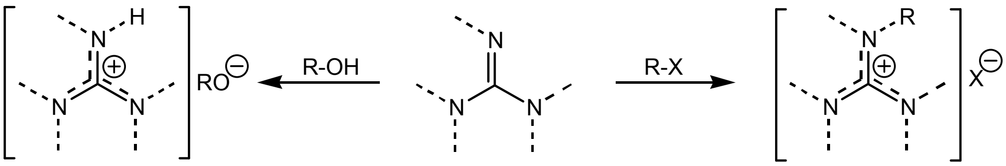
Today, ionic liquids have emerged as a promising alternative media to replace conventional organic solvents.[5-10] Their unique properties have already been demonstrated in a wide range of stoichiometric as well as catalytic reactions and many other special applications. However, the number of possible ionic liquids which can potentially be synthesized is difficult to estimate but can surely reach millions. The variation in their properties often realized by small changes in their molecular structure, provides an opportunity for their use in a number of applications. As an example, quite recently, the syntheses of new heterocycle-derived, energetic, low-melting salts were reported.[11,12] These salt compounds often possess advantages over non-ionic molecules since they tend to exhibit very low vapour pressures and high thermal stability. On the other hand, ionic species often exhibit higher densities than the corresponding non-ionic analogues. Among the alternatives studied and reported in literature, the imidazolium salts definitely dominate.

A special group of salts are ionic liquids based on substituted but both acyclic and cyclic guanidine or amidine derivatives as well as on phosphonium cations. This class of ionic liquids can be described as organosuperbase ionic liquids. Superbases, in particular cyclic guanidinium and amidinium derivatives with their strong basicity, are widely used as basic catalysts. Nevertheless, one main drawback of superbase catalysts in their free base form is associated to their difficult recovery from the reaction mixture post-synthesis. One feasible strategy is to convert these superbases into the ionic liquid form that greatly helps in recycling in the salt form.

2 Guanidinium ionic liquids

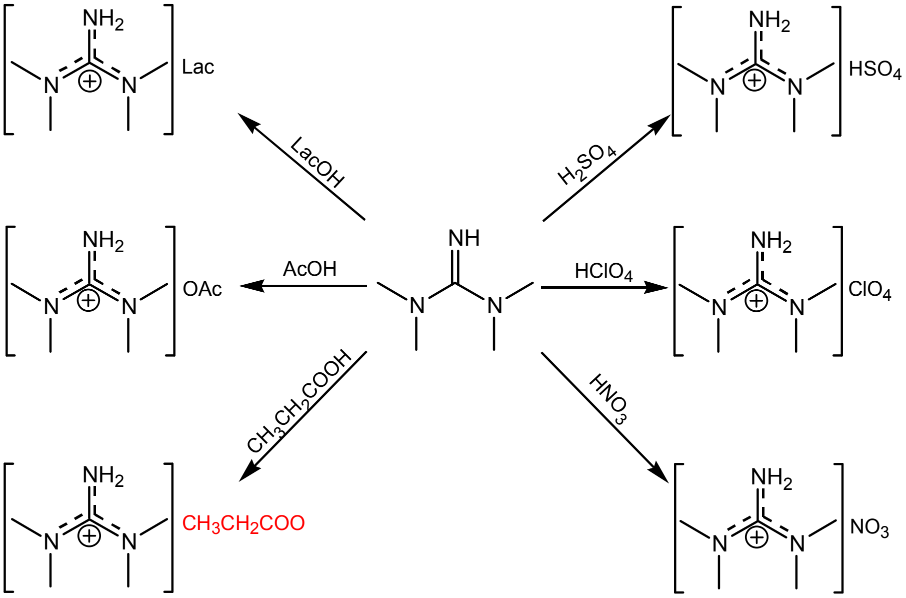
2.1 Acyclic guanidinium ionic liquids

One of the characteristic properties by which superbases (including also guanidine derivatives) are classified, is their particularly strong ability to capture hydrogen atoms. This relates not only to hydrogen with high acidity (e.g. mineral or organic acids), but also to e.g. hydrogen atoms with low acidity. In fact, guanidine may form salts when coupled to very weak protonic acids such as alcohols. For this reason, superbases are often called as "proton sponges". This means that acyclic guanidine derivatives can form two types of ionic liquids (Scheme 1). The first category includes protonated ionic liquids in a much broader sense than traditional ammonium salts whereas the second one is illustrated by classical ammonium salts obtained upon quaternization reaction of acyclic guanidine derivatives with various types of alkyl halides.



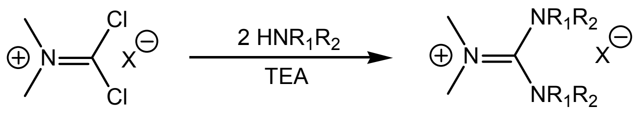
Scheme 1 Possible pathways for the synthesis of acyclic guanidinium ionic liquids

Upon synthesis of various guanidinium ionic liquids, the one most commonly used is 1,1,3,3-tetramethylguanidine (TMG). This important group of representative acyclic guanidine derivatives is easily available in industrial quantities. The easiness of obtaining protic guanidinium salts has inspired many researchers, thus facilitating the synthesis of protic ionic liquids based on TMG (Scheme 2).



Scheme 2 Main routes of synthesis of guanidine-derived protic ionic liquids

The synthesis of protonated guanidine ionic liquids (ILs) can be carried out under mild conditions simply by means of neutralization of guanidine with the corresponding protic acid. Protic ILs based on guanidine are characterized by their relatively high chemical and thermal stability. This stability arises from the stability of the guanidinium cation having a proton associated within the structure, leading to a guanidine framework with a strongly delocalized positive charge.[13] Consequently, ionic liquids containing the guanidine framework were first described by Mateus[14] and the synthesis strategy was based on the reaction of phosgene iminium chloride with secondary amines (Scheme 3).



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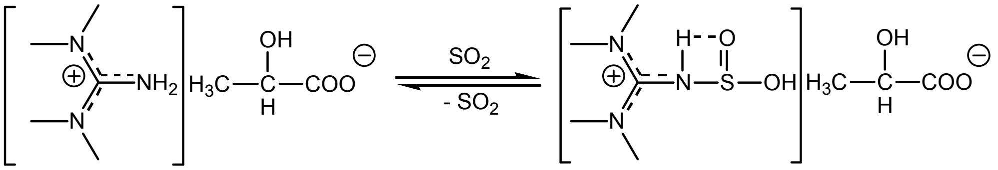
Scheme 3 Synthesis of alkyl guanidine ionic liquids

In 2004, both Jiang and Wilkes independently reported the synthesis of protic guanidinium ionic liquids [HTMG]Lac and [HTMG]TFA upon reaction 1,1,3,3-tetramethylguanidine with lactic acid (Lac) or trifluoroacetic acid (TFA).[15,16] Later on, [HTMG]Lac has been found to be useful since it is an effective homogeneous and recoverable catalyst in the Henry reaction[14], synthesis of β-hydroxyketone,[17] pyrane,[18] 3,4-dihydropyrimidinone,[19] thiazolidinedione,[20] aminothiophene,[21] cyanoacetylurea derivatives,[22] direct aldol condensation[23] as well as Michael reactions[24]. Further, it can also act as a promoter upon N-formylation of amines.[25] Still, [HTMG]Lac ionic liquids have been also found to be a very useful medium upon immobilization of Pd-nanoparticle catalysts onto a molecular sieve surface [26] as well as SO_2 capture from flue gases. The efficiency of SO_2 capture from gas mixtures is associated with the guanidinium molecule's particular ability towards SO_2 chemisorption. SO_2 chemisorption processes using guanidinium ionic liquids have been the subject of extensive studies[27-34] and the mechanism of SO_2 chemisorption on ILs, in particular [HTMG]Lac, has been studied both experimentally and theoretically. Han et al. demonstrated that the efficiency of SO_2 capture from a gas mixture is related to the specific reactivity of the guanidinium cation towards SO_2 in [HTMG]Lac ionic liquids.[35] It was suggested that SO_2 reacts with the N–H group in $[HTMG]^+$ cation whereupon a new N–S band was formed, thus theoretically allows chemical absorption of one mole of SO_2 by one mole of IL. Furthermore, Zhang et al. described new ILs based on the $[HTMG]^+$ cation and proposed a similar chemisorption mechanism.[36] Interestingly, Wu et al. reported, that [HTMG]Lac ionic liquid can chemically absorb only 0.5 mole of SO_2 per mole of IL, but they can physically absorb SO_2 when the molar ratio of SO_2 to IL is more than 0.5.[37] The chemisorption mechanism proposed by them is shown below (Scheme 4).[38]



Scheme 4 Proposed chemisorption mechanism of SO_2 into guanidine ionic liquids

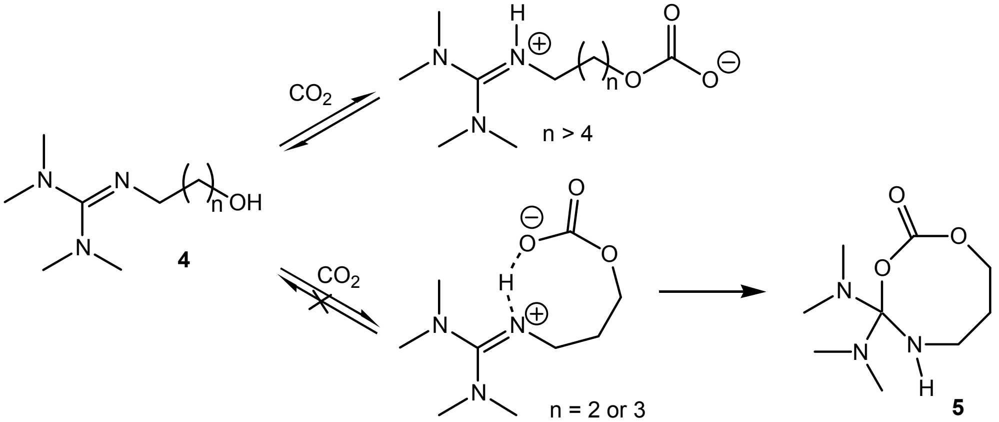
Interestingly, when attempting CO_2 chemisorption, the above reaction scheme is not valid when using simple ionic liquids based on TMG derivatives, .the plausible reason being the low acidity of CO_2. Significantly better CO_2 chemisorption capacity can be achieved using hydroxyalkyl guanidinium ILs **2**, **3** (scheme 5).[39-41]

2

3

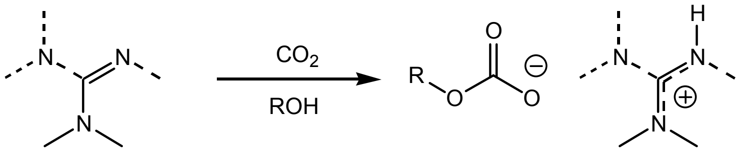
Scheme 5 Task-specific guanidinium ionic liquids

According to the mechanism described by Hildebrandt et al., in the case of hydroxyalkyl guanidine derivatives, chemisorption of CO_2 follows a completely different route than in the case of SO_2 chemisorption. In fact, it was claimed that the reaction is facilitated by the OH groups to form guanidium ionic liquids (Scheme 6).[39,40]



Scheme 6 Proposed mechanism upon chemisorption of CO_2 via hydroxyalkyl guanidinium ionic liquids

As reported by Hildebrant et al., in case of hydroxyalkyl guanidine **4** containing short hydroxyalkyl substituents (n<3), the reaction (chemisorption of CO_2) is not reversible. Thus, the CO_2 addition product easily cyclizes to a stable carbonate **5** that when heated up to temperatures approx. 100 °C does not release any of the chemically bound CO_2. In case of longer substituents (n> 4), the chemisorption of CO_2 is reversible. Instead of a stable cyclic carbonate, an unstable carbonate is formed that can easily release CO_2. An interesting and a more industrially feasible and practical alternative is to use TMG - alcohol mixtures upon chemisorption of CO_2, the reason being the easy availability of 1,1,3,3-tetramatyloguanidine (TMG) which is manufactured on industrial scale. The CO_2 chemisorption process using the TMG - alcohol systems proceeds according to a mechanism similar to that shown in Scheme 6 and leads to the ionic liquid **6** (Scheme 7).



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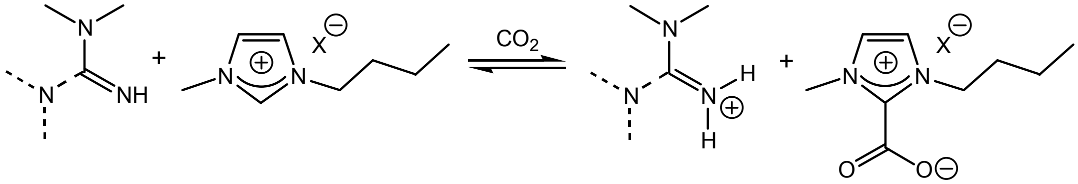
Scheme 7 Chemisorption of CO_2 via guanidine “switchable” ionic liquids

This type of ionic liquids are called "switchable" ionic liquids due to their rather straight-forward tendency to bind and release CO_2. The class of switchable ILs (SILs) was for the first time described by Jessop et al. upon introduction of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) based SILs.[42] It was also reported that the guanidine derivatives, in particular TMG, may also be used in this process.[42-48] In reality, instead of an alcohol, a classical imidazolium ionic liquid in an equimolar amount can also be used (Scheme 8), but the capturing capacity of the TMG SIL systems to chemisorb CO_2 was nearly two magnitudes of order lower compared to those based on TMG and an alcohol.[42,49]

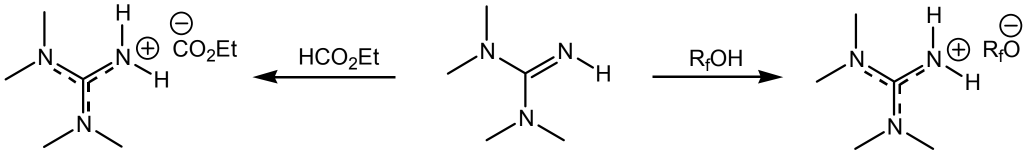


Scheme 8 Chemisorption of CO_2 via "switchable" guanidine–imidazolium, double ionic liquid system.

In another case, [HTMG]Lac was also used in conjunction to biocatalysis. Ebrahimi et al. described the results when two tetramethylguanidine-based ionic liquids in terms of the activity and stability of *Photinus pyralis* luciferase.[50,51] It was reported that the activity of the luciferase increased in the presence of [HTMG]Lac whereas in the presence of similar concentrations of the propionic acid derivate, [HTMG]PA, the activity decreased.

Protic ionic liquids derived from tetramethylguanidine and carboxylic acids (formic, acetic, propionic) as well as [HTMG]Lac have also found wide application in many areas of science. In particular, [HTMG]OAc that may be conveniently prepared via neutralization reaction between 1,1,3,3-tertamethylguanidine and acetic acid should be mentioned. Unlike many other protic ionic liquids like classical imidazolium ILs which are acidic in nature, protic ionic liquids based on guanidine derivatives are basic in nature and are, therefore, often used as base catalysts. Consequently, they are applied as an active catalyst or specific solvent in Henry [52] and Mannich reactions [53], aldol condensations [23] as well as many other condensation reactions involving amino groups.[54,55] Moreover, [HTMG]OAc has also turned out to be an efficient catalyst upon synthesis of piperidine, 1,3-indandione and pyrrolidyne derivatives – all important intermediates upon synthesis of pharmaceuticals [56], as exemplified as a specific catalyst upon synthesis of 6-aminouracil.[57] The same IL was also demonstrated as an active solvent upon Pd-catalyzed Heck reaction. Besides the solvent function, the IL also had a stabilizing function of the active catalytic complex taking advantage on hydrogen bonded Pd-IL system.[58] Many other protic ILs have been synthesized in an analogous way as [TMG]OAc and both organic acids like propionic acid (PA), isobutyric acid (iso-BA) and inorganic acids (HBF_4, HNO_3, $HClO_4$, or H_2SO_4) ~~acids~~ can be used.[59,60]

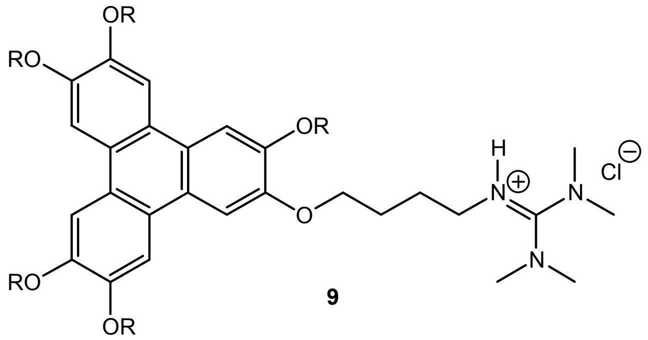
Likewise, all above introduced TMG -derived ILs ([HTMG]OAc, [HTMG]PA, [HTMG]iso-BA and [HTMG]TFA) turned out also to be highly active catalysts upon aldol condensation.[53] As yet as another example, [HTMG]PA among other ILs was also used in removal (dissolution) of epithelium from natural fibers (wool, silk).[61] However, the extraction/solubilizing ability of TMG-based ILs was outperformed by imidazolium ILs. Still, [HTMG]TFA was, in turn, a good catalyst upon synthesis of pyrane and 3,4-dihydropyrimidinone derivatives. [18,16] When aiming at hydrolysis of cellulose using water enriched with carbon dioxide as a reaction medium, [HTMG]HSO_4 performed well. [60] The incorporation of carbon dioxide enhanced the reaction rates significantly and gave rise to 26% and 72% yields of glucose and total reducing sugars (TRS), respectively. The adopted TMG ionic liquid was easily recovered and reused in four subsequent batches without any significant change in the catalytic efficiency. The particularly strong affinity of alkyl guanidine derivatives to proton capture has been taken advatange in synthesizing a number of new and task-specific protic ionic liquids (TSILs). They can be prepared by reacting 1,1,3,3-tetramethylguanidine with formic acid esters **7** [62] and even phenols or perfluorinated alcohols **8** (Scheme 9).[63,64] The strong basicity of the alkyl guanidine derivatives renders them viable to capture protons of relatively low acidity.



Scheme 9 Novel protic TSILs from TMG and fluoroalcohols or formate esters

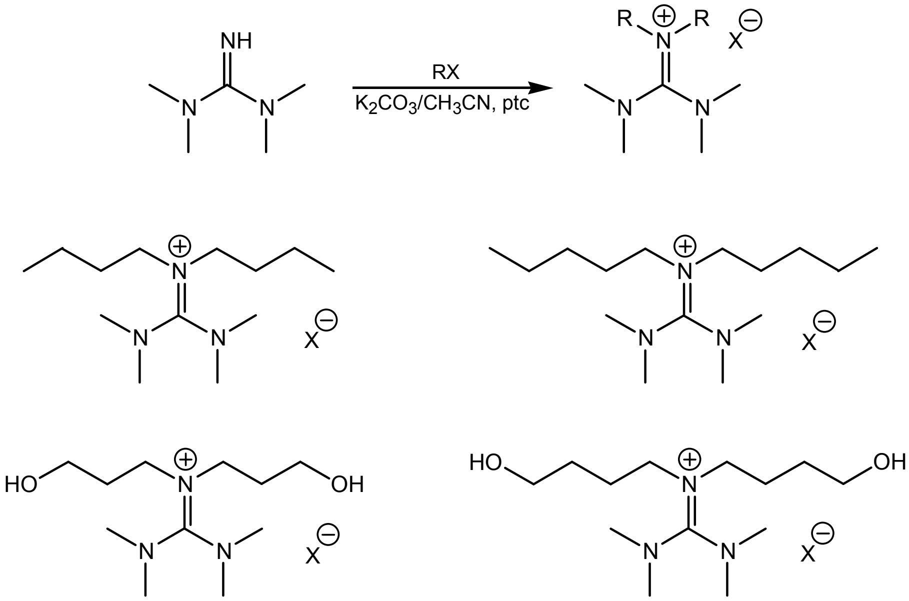
Consequently, the new protic ionic liquids obtained in this manner have been successfully demonstrated in CO_2 and SO_2 chemisorption (capture). According to the chemisorption mechanism, one SO_2 molecule reacts with the NH_2 group of the guanidinium cation whereupon a new SO_2H group is formed. The above new protic TSIL could capture SO_2 via both physical and chemical interactions, while even physical absorption does play an important role at experimental conditions.

The 1,1,3,3-tetramethylguanidine ILs described so far are usually prepared via synthesis strategies recognized as "classical". Anion exchange processes (metathesis) or protonation can undoubtedly be included into this category as well. If studying the literature, however, a number of cases of very specific ionic liquids obtained using unconventional methods can be identified. One such kind of example is represented by the species **9** containing an acyclic guanidine skeleton, but characterized by a more complex structure (Scheme 10) and described by Sauer et al.[65]



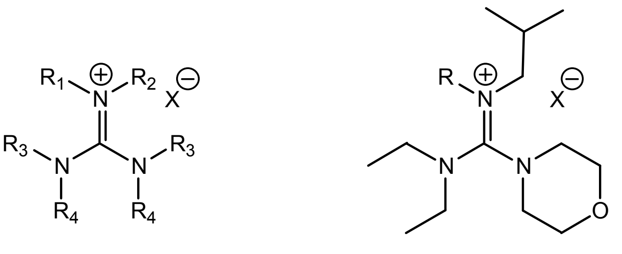
Scheme 10 Novel quaternary TSILs from TMG and a polyphenyl moiety

These new ionic liquids (**9,** R = C_5H_{11} - C_9H_{19}) have been successfully used as rectangular columnar mesophases. Further, Ding et al. describes the synthesis of series of novel ILs based on TMG using sequential alkylation and quaternization reactions ~~in sequel~~ (Scheme 11).[66,67]



Scheme 11 Synthetic route and examples of novel TSILs based on TMG

The above species were applied as selective extractants upon purification of proteins. Still, Zhang et al. used an efficient process to extract proteins with TMG acrylate[68] while a series of new guanidinium ionic liquids was developed by Shah et al.[69-71] Both hexaalkyl guanidinium ILs **10** and **11** (Scheme 12) and also specific, aminoacids-derived chiral ILs with the guanidinium framework **12** and **13** (Scheme 13) have been synthesized.



10 **11**

Scheme 12 Novel TSILs - alkyl guanidinium ILs

Another novel symmetrical and unsymmetrical hexaalkylguanidinium ILs **10** have been also described by Bogdanov et al.[72,73] He studied effect of alkyl substituents and type of anions on density and solubility properties.

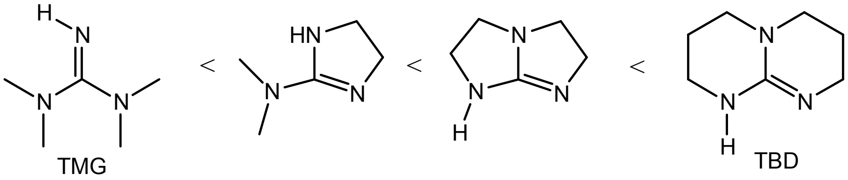
12 **13**

Scheme 13 Chiral aminoacid guanidinium ILs

TMG derived ionic liquids can also used as solvents in olefin epoxidations. Gharnati et al. synthesized a series of quaternary guanidinium ionic liquids, both well-known variants with BF_4 (tetrafluoroborate), PF_6 (hexafluorophosphate), NTf_2 (bis(trifluoromethylsulfonyl)amide) or CF_3SO_3 (triflate) anions as well as the new phosphotungstate anion.[74] In case of selected olefins, conversions exceeding 90% were achieved. As reported, the performance was, however, *in par* with analogous imidazolium ionic liquids. Yet another interesting application of guanidinium ILs is described by Mamontov et al.[75,76] It was reported that TMG-based ILs can be used as efficient fuel cell electrolytes. In another case, a series of new type of guanidinium ILs applicable as fuel cell electrolites have been claimed by the Nippon Steel Chemical Co. Ltd. [77] Further, guanidinium ILs as possible electrolytes for lithium-ion batteries were suggested by Hess et al. [78] In this case, the performance was comparable to well-known carbonate-based electrolytes or pyrrolidinium-based electrolyte ILs. Also, Zhao et al. carried out detailed studies of the specific conductivity of guanidinium ILs. [79] It was concluded that design of small symmetrical guanidinium cations with high proton delocalization are crucial in terms of achieving good conductivity characteristics for guanidinium ILs.

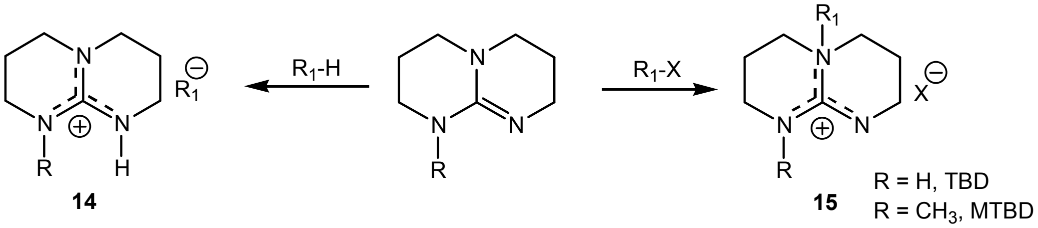
2.2 Cyclic guanidine ionic liquids

Cyclic guanidine derivatives are a very special class of strongly basic species. Theoretical studies encompassing the physicochemical properties of various guanidine organosuperbases have shown that the basicity of guanidine derivatives decreases as follows (Scheme 14): [4,80]



Scheme 14 Basicity of guanidine derivatives

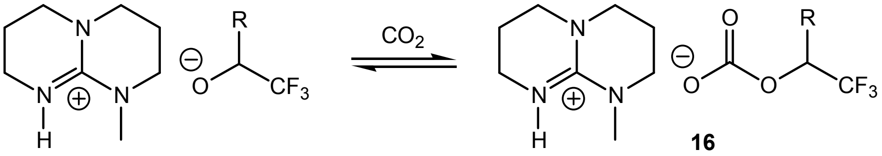
The substituted guanidine derivatives, wherein guanidine framework N = C (N) - N is introduced into the rigid bicyclic systems are characterized by their interesting physicochemical properties which distinguish them from the corresponding acyclic analogs. The specific properties of cyclic guanidine derivatives were described in detail by Coles. [81] As compared to acyclic guanidines, cyclic guanidine derivatives are also less influenced by steric effects that in case of acyclic guanidine derivatives often play an important role. Cyclic guanidine derivatives are widely applied in the synthesis of several task-specific catalysts and also find use as ligands in organometallic catalysts. Among the many described cyclic guanidine derivatives the most important are derivatives of dec-5-ene. Like TMG, cyclic guanidine derivatives, in particular 1,3,5-triazabicyclo[4.4.0]dec-5-ene (TBD) and its methyl analogue, MTBD, can be used as cation precursors of various ionic liquids, both protic **14** and quaternary alkyl guanidinium ones **15** (Scheme 15)



Scheme 15 Synthetic routes leading to TSILs based on cyclic guanidine derivatives

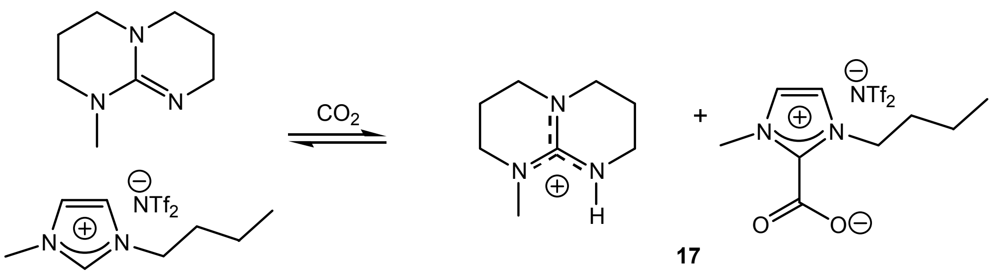
Examples of ILs based on cyclic guanidines are much harder to find due to the substantially higher price of the cyclic guanidine derivatives compared to e.g. TMG. Nevertheless, TBD and MTBD, as along with acyclic guanidines, are potent SIL precursors when aiming at CO_2 capture processes. As reported by Jessop et al., both TBD and MTBD are characterized by their extremely high basicity and can, therefore, deprotonate weakly dissociated molecules like ethylene glycol.[47]

The use of TBD and MTBD in "switchable" CO_2 capture systems has been a subject of several studies.[47, 71-80, 82-87] Indeed, chemisorption of CO_2 can be facilitated by specific protic ionic liquids based on MTBD and fluoroalkohols **16** (Scheme 16).



Scheme 16 Mechanism of CO_2 chemisorption by MTBD-perfluoroalcoholate ionic liquid [82]

and switchable ionic liquids systems based on MTBD and imidazolium ionic liquids **17** (Scheme 17).



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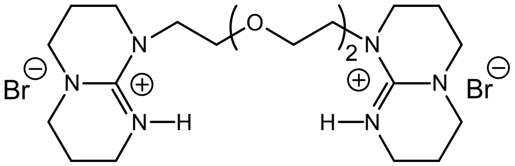
Scheme 17 Mechanism of CO$_2$ absorption by [bmim][NTf$_2$]-MTBD system[83]

The highest CO$_2$ uptake capacity of 1.13 per mole of IL was achieved for the protic ionic liquid [MTBDH][TFE] (TFE = trifluoroethanol). In turn, in case of gemini IL [MTBDH]$_2$-[HFPD], built from MTBD and 2,2,3,3,4,4-hexafluoro-pentan-1,5-diol, a higher CO$_2$ capacity of more than 2.0 mole per mole of IL was achieved, obviously due to presence of two CO$_2$-reactive groups.[82-84] As reported by Dai et al., the influence of different proton donors upon CO$_2$ chemisorption is particularly important. It was clear that the absorption was almost complete within 5 min in case of the IL with trifluoroethanolate anion, whereas the system forming the zwitterionic imidazolium upon CO$_2$ uptake, complete CO$_2$ saturation was observed only after 30 min. In contrast, the chemically neutral IL like [MTBDH][NTf$_2$], could uptake 0.02 moles of CO$_2$ per mole of IL only. To assess the strength of CO$_2$ chemisorption, FT-IR analysis is very useful. In a reaction system [C$_4$MIM][NTf$_2$]-MTBD + CO$_2$, a new band assigned as a carboylate group appears at 1669 cm^{-1}. The high CO$_2$ capturing capacity of SILs (switchable ILs) based on superbases, in particular TBD or MTBD, has been already exploited in processes that consume CO$_2$ as a key reagent.[85-87] Thus, Foltran et al. studied the synthesis of cyclic carbonates via coupling of CO$_2$ with epoxides.[85] It was concluded that the nucleophilicity of IL anion bears a great importance in terms of the efficiency of this reaction. It turned out that the best results were achieved with the protic [HTBD]Br IL. Similar studies were also conducted by Yang et al. [86,87] and, as the first step, cyclic carbonates were obtained upon coupling of CO$_2$ with epoxides. As the next step, methyl carbonates were obtained via a transesterification reaction with methanol. Moreover, several Lewis basic ionic liquids were tried as catalysts, including various TBD ILs and a new gemini IL with the TBD moieties interconnected by a polyoxyethylene spacer **18** (Scheme 18).[87]



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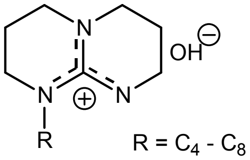
Scheme 18 New gemini TBD-derived IL [87]

It is evident that the presence of tertiary nitrogen atoms in the gemini-type cation of [TBD-PEG-TBD] obviously promote the moieties ability to activate methanol, thus leading to high transesterification rate of ethylene carbonate with methanol. The advantage of the use of basic ionic liquid, Br[TBD-PEG-TBD]Br, as catalyst, is the integration of cycloaddition and transesterification processes in a single process. TBD ionic liquids have been recently applied as catalysts in the N-formylation of amines. Baghbanian et al. reported that for amine, formic acid and TBD ILs reaction systems, respectively, corresponding formamides can be prepared in good to excellent yields.[88,89] The best results were obtained in case of [TBD]TFA ionic liquid. Furthermore, this IL was easily separated from the product and reused a number of times without any significant loss in activity. Recently, Nowicki et al. synthesized for the first time the new basic ionic liquid [TBD-Bu]OH **19** (Scheme 19).[90]



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Scheme 19 New basic alkylguanidinium IL [90]

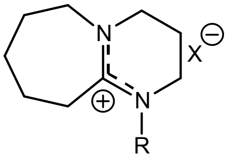
This new type of IL is unusual since the cation is able to cope with the strongly ~~alkaline~~ basic OH anion whereas e.g. the imidazolium cation would unavoidably slowly decompose. The [TBD-

Bu]OH was successfully used as a basic catalyst upon transesterification of fatty acid methyl esters with polyols (neopentyl glycol, trimethylolpropane (TMP). Moreover, the IL has a good thermal stability and can be applied in various transesterification processes. The highest FAME conversion (83%) was obtained upon synthesis of the TMP ester of oleic acid over the [TBD-Bu]OH catalyst. Snyder et al. studied oxygen reduction process over nanoporous NiPt alloy nanoparticles using hydrophobic, protic ionic liquid based on MTBD and *bis*(perfluoroethylsulfonyl)imide anion [BETI].[91] The IL was incorporated into the pores of nanoporous nanoparticles (NP) residing inside a high surface area NiPt alloy. It was concluded that the NP-NiPt/C+[MTBD][BETI] encapsulated catalyst is more active than commercial Pt/C. Kondo et al., in turn, studied the influence of the molecular structure of TBD derived protic ionic liquids in terms of their tribological and thermal properties.[92] It was concluded that the newly developed TBD ILs were adsorbed on surfaces highly orientated structures. The stronger adsorption due to the intensive adhesive interaction of a polar group is necessary in friction reduction. Moreover sufficient length of the hydrocarbon chain causes an extensive cohesive interaction that compensates for mechanical durability.

3. Amidinium ionic liquids

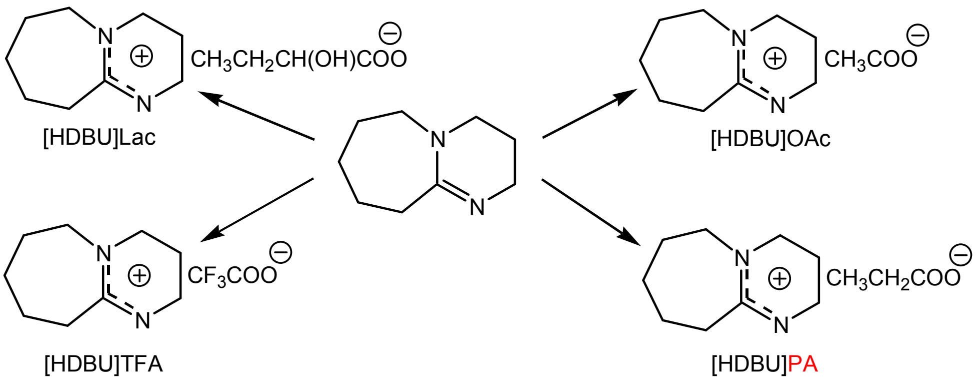
3.1 DBU ionic liquids

Among the amidine derivative superbases, two cyclic amidine derivatives are of particular importance: 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). As described above, guanidine derivatives DBN and DBU are manufactured on a technical scale since their strongly basic properties are widely taken advatange of in many areas of chemistry and other application areas.[93] Like guanidine derivatives, cyclic amidine derivatives can also be used as starting materials for the synthesis of ionic liquids. In particular, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has been given wide attention. First DBU ionic liquids were described in 2004 by Braun in patent literature[94] and later by Tolstikova and Shainyan.[95] The advantages of DBU as an IL precursor are associated with the properties like its large size, low symmetry of the cation formed and strong charge delocalization on the N-C=N structure. Consequently, ionic compounds with low melting points can be synthesized (Scheme 20).



Scheme 20 General structure of alkyl DBU ionic liquids

Most of above mentioned ILs are neutral and typically applied as reaction solvents. More recently, a new class of task-specific DBU-derived ILs applicable not only as solvents but, at the same time, as catalysts or promoters was developed. These new protic ILs can be synthesized by a simple neutralization reaction of DBU by the corresponding carboxylic acids, including acetic, lactic, propionic or trifluoroacetic acid (Scheme 21). The [HDBU]TFA IL can be classified as a weak acid, whereas [HDBU]OAc, [HDBU]PA and [HDBU]Lac ILs are weak basic.



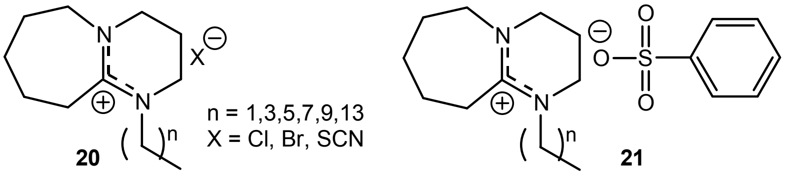
Scheme 21 Main routes of synthesis of DBU-derived protic ionic liquids

Protic DBU ILs, in particular [HDBU]OAc, [HDBU]PA and [HDBU]Lac, were widely used as catalysts and promotors in base catalyzed Michel condensations.[96-98] It was reported by Chen et al., [HDBU]OAc performed slightly better in their model reaction than the other DBU-derived protic ionic liquids. Under optimal reaction conditions, 95% yield of the addition product was obtained.

Also, the reactivity of DBU (free base) as a promoter, in acetonitrile and at room temperature, was compared for this particular model reaction (between dibenzylamine and methyl acrylate).[98] It turned out that [HDBU]OAc outperformed free DBU, albeit the difference was small. An analogous process has been Also for a series of cyclic nitrogen nucleophiles (morpholine, piperidine, 1-methyl-,1-ethylpiperazine and pyrazole), an analogous process was studied.[99] Using methyl acrylate as the substrate, the [HDBU]OAc catalyzed aza-Michael conjugate reaction resulted in excellent yields of Michael adducts, at ambient temperatures, under solvent-free conditions and in short reaction times. The [HDBU]OAc IL could be recycled at least six times without any considerable loss of activity. Unexpectedly, it turned out that even though this IL is a weaker base than the DBU, its catalytic properties were better tuned for aza-Michael reaction. Similar results were reported in case of aromatic amines. Although DBU is a potent catalyst in aza-Michael additions, significant amounts of bis-addition products were obtained as by-products. When a protic DBU ILs such as [HDBU]OAc, [HDBU]PA or [HDBU]Lac were the catalysts of choice, no bis-addition products were observed and 89-99 % yields with good chemo- and regioselectivity were obtained upon coupling of aniline and ethyl vinyl ketone. Other base catalyzed systems like Knoevenagel condensation of various aromatic aldehydes with ethyl cyanoacetate and malononitrile worked as well and under mild and solvent free conditions.[100,101] Herein, all tested ILs were characterized by their high catalytic activity, in particular [HDBU]Lac. Also aromatic aldehydes bearing electron withdrawing groups could be coupled with ethyl cyanoacetate, albeit affording lower yields of the target products.

The recycled ionic liquid was reused in subsequent batches and could be recycled six times without any considerable loss of activity. Also Chen et al. studied DBU based protic ionic liquids as catalysts upon reaction of benzaldehyde with ethyl cyanoacetate in water, at room temperature.[101] Under such, more “green” conditions, a very high yield of desired products was obtained. Among the previously described protic ionic liquids, the use of [HDBU]OAc resulted in the highest catalytic activity. Thus, the yield of the condensation product was 95%. This synthesis protocol has many advantages, such as high product yields, "green" reaction medium, ease of work-up, feasible reuse of the IL on a large scale; in summary, application of this IL in industrial scale is feasible. Shaterian et al. reported the efficient synthesis of 1,4-dihydropyrano[2,3-c]pyrazole derivatives in the presence of a reusable, weakly basic [HDBU]OAc ionic liquid as the catalyst. Moreover, the reaction proceeds under one-pot, solvent-free conditions at room temperature and gives rise to a high yield.[102] The advantages of this synthesis strategy are: good yields, short reaction time and a simple work-up procedure. Patel et al. reported a simple and efficient synthesis protocol of imidazo[1,2-a]quinolone derivatives from enaminone, various aldehydes or ketones and malonitryle, catalyzed by [HDBU]OAc under acoustic cavitation (ultrasonic irradiation) using methanol as co-solvent.[103] Still, [HDBU]OAc has also been used as a catalyst in one-pot synthesis of new, fluorescent triazolyl spirocyclic oxindoles under acoustic cavitation.[104]

In addition to the "classic" protic ionic liquids such as [HDBU]OAc, several other "task-specific" ILs (TSILs) derived from DBU have been synthesized (see **20** and **21;** Scheme 22).[105,106]

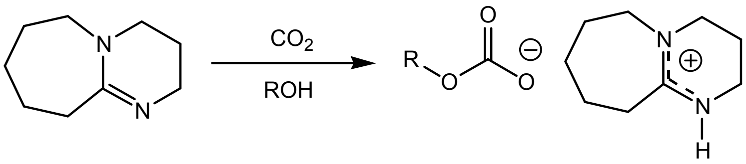


Scheme 22 An overview of the new task-specific DBU ionic liquids

Lethesh et al. described a series of new DBU-derived ILs.[105] In this case the ILs were synthesized following a one/two-step protocol. In the first step, C_2 - C_{14} N-alkyl DBU halides (Cl or Br) were obtained, which in turn were converted into corresponding thiocyanate ILs (step two). Physicochemical properties of these new ILs were fully determined. They also studied how the alkyl chain length and the operation temperature influenced on the physical properties of the ILs. Wu et al., in turn, described a very efficient protocol for the conversion of glucose into 5-

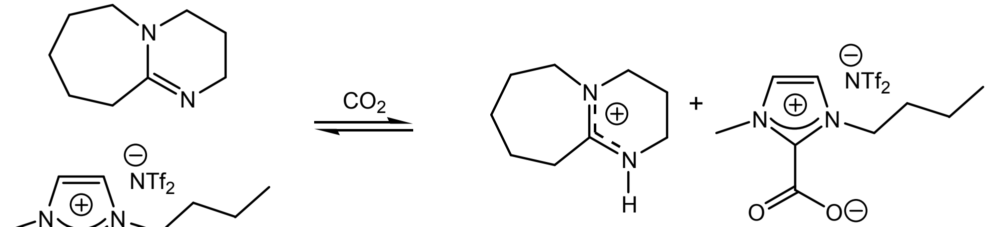
hydroxymethylfurfural in DBU-derived ionic liquids containing benzenesulfonate anion (Scheme 22).[106]

A very important and intensively studied application area of DBU ionic liquids is CO_2 and SO_2 chemistry, in particular CO_2 chemistry. This process can be shortly described as a two-step route: capture/activation and subsequent conversion. Carbon dioxide obtained upon combustion of fossil fuels is considered as one of the most powerful greenhouse gases. The conventional industrial technology in the capture of CO_2 is chemical absorption in aqueous amine solutions. The approach is characterized by low cost, high absorption efficiency and capacity. However, the use of aqueous amine solutions also gives rise to serious problems e.g. loss of solvents by evaporation, corrosion problems and high energy consumption. Certain ionic liquids, in particular amidine (DBU, DBN) ILs, that are designed as Lewis acid and Lewis base combinations, might be able to activate CO_2 molecules and simultaneously interact with second reagents. DBU ILs are particularly often explored in CO_2 chemistry processes. Davis et al. reported first chemisorption of CO_2 employing an amino-functionalized task-specific imidazolium ionic liquid. His results showed that 0.5 mole CO_2 can be captured per mole of IL with a capacity of about 7% (w/w). The capture was complete in 3 h and under ambient pressure.[107] During the following years, alternative strategies relying on an entirely different classes of ILs was developed. The major improvement was that CO_2 capture was rapid and reversible but could also retain a higher loading of CO_2. The new protocol was based on protic superbase, "switchable" ionic liquids (SILs) derived from, in particular, DBU. The concept of switchable ILs was introduced by Jessop et al. for 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[42] Research in CO_2 chemistry using DBU ionic liquids was later extensively developed by Jessop and Hildebrant and recently by Mikkola et al. According to Jessop's and Hildebrant's studies, the chemisorption of CO_2 follows a similar mechanism in protic, switchable DBU-derived ILs as in the case of guanidinium ILs (Scheme 23).[42-45,108-110]



Scheme 23 Chemisorption of CO_2 into DBU "switchable" ionic liquids

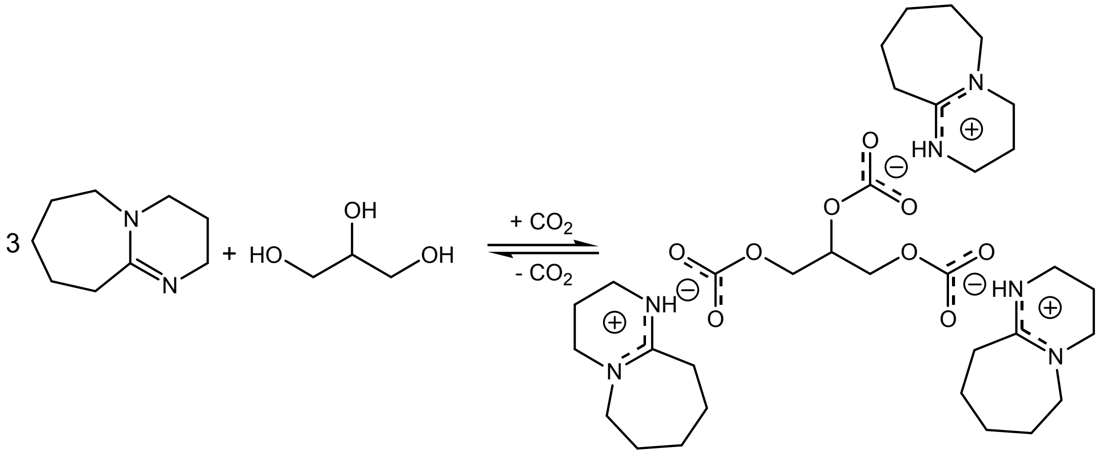
DBU alkylcarbonate salts, prepared via bubbling of CO_2 through equimolar mixtures of DBU and lower alcohols such as ethanol and methanol, are solids at room temperature. However, alkyl carbonates formed from DBU and 1-propanol, 1-butanol, 1-hexanol, 1-octanol, or 1-decanol are viscous liquids at room temperature and can be converted back to a neutral mixtures of organic liquids upon bubbling of nitrogen or argon or, alternatively, via heating.[45] As proton donors, also fluoroalcohols can be used.[111] Still, instead of alcohols, neutral imidazolium ILs can be used as proton donors (Scheme 24).[112-114]



Scheme 24 Mechanism of CO_2 absorption in a $[C_4mim][NTf_2]$-DBU system

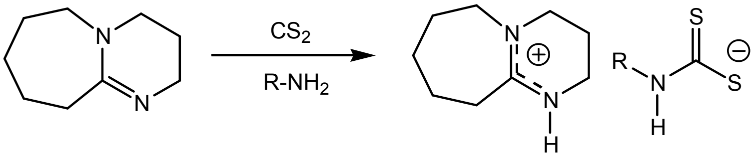
Yang et al. introduced a new CO_2 capture protocol by DBU-functionalized ionic liquids through Li^+-stabilized zwitterionic adduct formation. He reported that $[DBULi]NTf_2$ ionic liquid exhibited a CO_2 capacity of 0.75 mole CO_2 absorbed per one mole of base. The reason is the drastically increased viscosity of the IL as a function of increasing amounts of absorbed CO_2. This is much higher CO_2 loading than what can be achieved by a conventional 1-hexyl-3-methylimidazolium hexafluorophosphate IL.[115] According to conclusions reported by Jessop, the decomposition temperatures of DBU alkylcarbonates (Scheme 24) are between 50 - 60 °C. It is obvious that application of these carbonate salts could be limited from the industrial point of view. Later on

Mikkola et al. developed a strategy leading to SILs that give rise to efficient CO_2 capture.[116-118] As proton donors, several hydroxyl-functionalized derivatives such as glycerol and various aminoalcohols were used. From an industrial point of view, glycerol has many advantages. It is cheap and renewable feedstock obtained e.g. as a by-product of biodiesel production. In the presence of equimolar amount of amidine, in relation to OH, it forms carbonates similar to alcohols (Scheme 25).



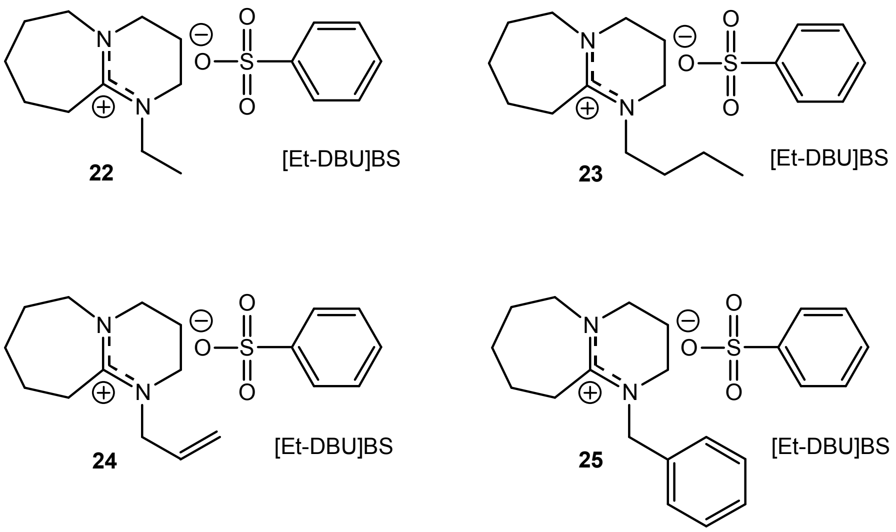
Scheme 25 Chemisorption of CO_2 by DBU -derived "switchable" glycerol ionic liquids [118]

In-depth study of this process showed that the viscosity of switchable ILs is an important parameter: the mass-transfer process has a crucial impact. Beside glycerol, selected alcohols and aminoalcohols (prolinol, valinols and aminohexanols) were demonstrated as proton donors.[119] An increase in viscosity was observed for all the studied switchable ionic liquids. High efficiency and fast sorption/desorption kinetics (CO_2 capture and release) were observed for 1-hexanol and 6-amino-1-hexanol. Analogously to the process of CO_2 capture occurring in switchable DBU ionic liquids, also SO_2 [119,120] and CS_2 can be sequestrated.[121] In the case of CS_2, instead of alcohols, aliphatic amines were used (Scheme 26).



Scheme 26 Chemisorption of CS_2 via DBU "switchable" ionic liquids

The amidinium dithiocarbamates are thermally more stable than their amidinium carbamate analogues. The DBU dithiocarbamates are more stable at higher temperatures than corresponding amidine-amine mixtures, even under normal air atmosphere. Unlike their amidinium carbamate analogues, the amidinium dithiocarbamates do not lose the CS_2 molecule under heating above their decomposition temperatures (ca. 80 °C). Moreover, various CO_2 chemisorption processes are widely used, not only in the capture of CO_2 from flue/waste gases but also as the first step in various CO_2 valorization processes. Yang et al. described the synthesis of a series of new Lewis basic ILs applicable in the synthesis of cyclic carbonate from epoxide and CO_2. The reaction occurs at low pressure and under solvent-free conditions.[87] It was found that the [HDBU]Cl ionic liquid gives rise to the highest catalytic activity upon conversion of CO_2 and almost a quantitative yield of 97% as well as 99% selectivity to cyclic carbonate was obtained. Zhang et al. described the carbonylation of o-phenylenediamines with CO_2 to 2-benzimidazolones catalyzed by a DBU-derived IL under mild and solvent-free conditions.[122] Thus, [HDBU]OAc gave rise to a high catalytic efficiency and a series of benzimidazolones were obtained with high yields. It was demonstrated that [HDBU]OAc exhibits a bi-functional character in this chemical case. It was proposed that the cation was activating CO_2 whereas the anion was activating o-phenylenediamines. As yet an interesting case, Wu et al. described a series of DBU-based new ILs with benzenesulfonate cation **22-25** (Scheme 27).[123]



Scheme 27 Overview of the new task-specific benzenesulfonate DBU ionic liquids [123]

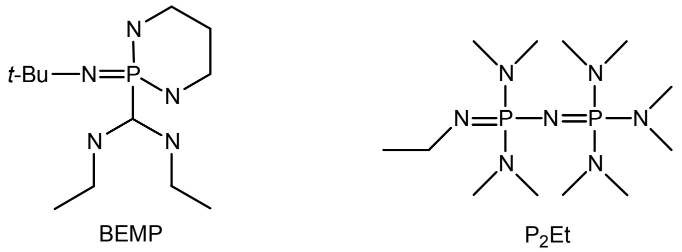
The above ILs were used as solvents upon synthesis of HMF from glucose in the dehydration process catalyzed by $CrCl_3$. In the Et-DBUBS/$CrCl_3$ catalytic system, 83.4% yield of HMF was achieved. Singh et al., in turn, reported ultrasound promoted, one-pot synthesis of novel fluorescent triazolyl spirocyclic oxindoles in DBU-derived task specific ionic liquids. [124] In case of [HDBU]Ac and DBU-Bu]OH ILs, the desired spirocyclic oxindoles were obtained in high yields of 94%. Moreover, Chen et al. reported the use of protic ILs [HDBU]C_2H_5COO, [HDBU]C_3H_7COO and [HDBU]C_4H_9COO as the reaction medium in Ni-Raney catalyzed transfer hydrogenation of nitriles with potassium formate as the hydrogen donor.[125] In the studied reaction, the highest yield of the corresponding amines was achieved in [HDBU]C_4H_9COO IL milieu. As was the case with TBD, alkylamidinium hydroxides have also been prepared using DBU as the precursor.[90] Consequently, new basic ILs were applied as base catalysts upon transesterification of FAME with polyols, but their catalytic activity was significantly lower than what was achieved in case of TBD alkylguanidinium hydroxides. DBU-derived ionic liquids can be considered both as catalysts and as well as reaction environments (solvents) demonstrating versatile applicability. Kondo et al. described the synthesis of new protic ionic liquids based on DBU and selected carboxyclic acids. Moreover, their tribological and thermal properties were determined.[92] Mahajan et al. described the synthesis of a series of novel DBU-derived, surface active (surfactant) ionic liquids.[126] The new, cationic surface active ionic liquids (SAILs) derived from DBU were prepared through quaternization of DBU with selected alkyl bromides. Still, their aggregation behavior was examined by surface tension and conductivity measurements. In addition, DBU ionic liquids have also been used in biomass processing. For example, Samori et al. studied liquid-liquid extraction of lipids from *B. braunii* algal biomass samples using switchable DBU-octanol and DBU-ethanol systems.[127] It was reported that the DBU-octanol system gave rise to the highest yield of extracted hydrocarbons from both freeze-dried and liquid alga samples (16% and 8.2%, respectively, contra 7.8% and 5.6%, respectively with n-hexane). Further, D'Andola et al. developed a series of DBU-derived ionic liquids, both protic and quaternized alkylamidine ILs with halogen, formate and acetate anions.[128] The synthesized ILs were excellent solvents for cellulose. As reported by Diop et al., DBU-derived alkylamidinium ionic liquids are also excellent lignin solvents.[129] Still, an extensive study in biomass processing was conducted by Mikkola et al.[130-136] In an earlier study, a family of new SILs from CO_2 as well as a mixture of DBU and $C_4 – C_6$ alcohols were prepared and applied in a selective extraction of hemicelluloses from spruce wood.[131] In case of the hexanol-SIL, 12 wt.% the weight reduction of the milled spruce was achieved, while in case of the butanol SIL, the corresponding value was 10 wt.%. In a further study on the fractionation of cellulosic biomass, other switchable ILs were synthesized from alkanolamines or glycerol, DBU and CO_2.[134-136] It was demonstrated that the treatment at 120 °C of birch chips with a SIL synthesized from DBU, monoethanolamine and CO_2, resulted in a 23% weight reduction in 24 h. At the same time, 82 wt.% of hemicelluloses and 90 wt.% of lignin was removed. Later on, a new switchable ionic liquid derived from DBU, alkanolamine and SO_2 was used in the fractionation of wood biomass.[136] Using the "short time and higher temperature" (STHT) protocol, selective dissolution of mainly lignin occurred. It was successfully demonstrated that both hard and soft wood can be fractionated at a very short processing time (c.a. 2h) at 160 °C.

3.2. DBN ionic liquids

Although similar to DBU in basicity, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) is far less popular as a starting material upon synthesis of ionic liquids. A number of DBN ionic liquids have been described in patent literature.[94] Moreover, Hummels et al. reported that protic [HDBN]OAc IL seemed to be an excellent solvent upon production of cellulosic fibres with strength properties significantly higher than those of other man-made commercial fibres.[137,138] Still, [HDBN]OAc IL has also been used as a solvent in a cellulose functionalization process[139] and as a solvent in cellulose acetylation.[140] Consequently, when using the recyclable [HDBN]OAc IL, oxypropylation of cellulose was obtained and a better product quality and cleanliness was observed than imidazolium [emim][OAc] IL was the solvent. Wahlström et al. reported the results on hydrolysis of cellulose with *Trichoderma reesei* Cel5A in the presence of the new DBN ionic liquid.[141] In this process, two protic amidinium ILs were studied, [HDBN]OAc and [HDBN]PA but also the DBN dimethylphosphate IL. It was concluded that the new superbase ILs did not differ in terms of cellulose compatibility from the common imidazolium ILs. In case of phosphonium DBN ionic liquid, the hydrolysis yield was comparable to protic guanidinium ILs ([HTMG]PA, [HTMG]BA) but lower than in the case of an imidazolium IL ([emim]OAc). Finally, DBN ionic liquids have also been applied in CO_2 capture by tertiary amidine-functionalized ionic liquids through Li^+-stabilized zwitterionic adduct. It was reported that the CO_2 capturing capacity of [DBNLi]NTf_2 was higher than that for the corresponding DBU or imidazolium ILs and comparable to TMG ILs. [116]

4. Other organosuperbases ionic liquids

Among various organosuperbases utilized as precursors for ionic liquid synthesis, only selected phosphazenes have been tried. Phosphazene-derived ionic liquids, beside other superbase ILs, were also applied in CO_2 processes in line with the switchable ILs protocol. Indeed, Wang et al. tried two different phosphazene bases (Scheme 28).[82-84]



Scheme 28 Superbase phosphazene ILs applied in the CO_2 capture process

The highest CO_2 uptake capacity (close to equimolar) was demonstrated by P_2Et/[bmim]NTf_2 switchable ionic system. Slightly lower, 0.86-0.96 capacity, was observed when imidazole or N-methylpyrrolidone were used as proton donors. The lowest CO_2 capacity of 0.49-0.81, was observed for BEMP/[hemim]NTf_2 and P_2Et/[hemim]NTf_2 switchable systems.

5. Conclusions

This paper we gives a comprehensive review of various task-specific ionic liquids derived from TMG, TBD, DBU, DBN and other superbase-derived ionic liquids. Being in compliance with current trends that arise in relation to ionic liquids, the term "superbase-derived ionic liquid" has been treated much more broadly than it is commonly understood. Classically interpreted synthesis of ionic liquids is understood as a reaction, usually quaternization or protonation of the nitrogen atoms present in free bases leading to compounds with ionic structure. Reports published in recent years allows for an extension of this definition to "switchable" ionic liquids that are formed under the reaction conditions with the appropriate reagents, but can be decomposed to the mixture of starting reactants and be used again. This strategy relying on superbases, has been widely used in capture and activation of CO_2, SO_2 as well as also in COS processes. Due to its great practical importance, it is evident that this approach is still under development. In general, organosuperbase-derived ionic liquids demonstrate relatively higher specific catalytic activities compared to many other popular ionic liquid as well as much better chemo- and steroselectivities, favorable recovery and reuse properties and excellent recyclability.

Acknowledgements

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Abbreviations

TMG - 1,1,3,3-tetramethylguanidine

DBU - 1,8-diazabicyclo[5.4.0]undec-7-ene

DBN - 1,5-diazabicyclo[4.3.0]non-5-ene

TBD - 1,3,5-triazabicyclo[4.4.0]dec-5-ene

MTBD - 7-methyl-1,3,5-triazabicyclo[4.4.0]dec-5-ene

TSIL - task specific ionic liquids

SIL - switchable ionic liquids

OAc - acetate

Lac - lactate

TFA - trifluoracetete, triflate

NTf_2 - *bis*(trifluoromethylsulfonyl)imide

BF_4 - tetrafluoroborate

PF_6 - hexafluorophosphate

BS - benzenesulfonate

HMF - 5-(hydroxymethyl)-2-furaldehyde

TMP - trimethylolpropane

PEG - *poly*(oxyethylene) glycol

FAME - fatty acid methyl esters

BETI - *bis*(perfluoroethylsulfonyl)imide

STHT - “short time and higher temperature” protocol

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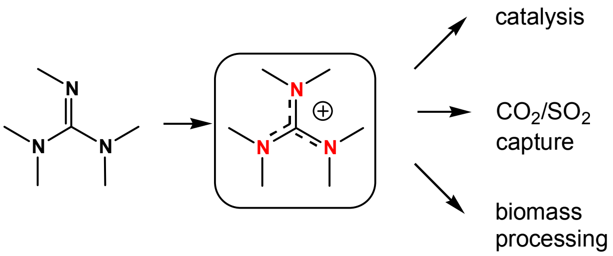
Ionic liquids derived from organosuperbases: en route to “superionic” liquids

Janusz Nowicki, Marcin Muszyński and Jyri-Pekka Mikkola



This review presents a comprehensive review of various task-specific ionic liquids derived from TMG, TBD, DBU, DBN and other organosuperbases.