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DBU-Based Ionic Liquids



Zhen Li

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou, China

Introduction

DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) is a strong tertiary amine base (pH 12.8) with a double heterocyclic structure, which has been widely used in organic synthesis. The two *N* atoms in the molecule have sp^2 , sp^3 hybrid state, respectively. Both *N*1 (sp^3) and *N*8(sp^2) have a pair of lone electrons exposed in different directions (Scheme 1).

Medina et al. [1] demonstrated that when DBU reacts with equimolar amounts of water, it undergoes protonation at the *N* atom and transforms into a second resonance structure (Scheme 1). This second resonance structure of DBU has Brønsted basic properties and is therefore responsible for the catalytic activity in aldol condensation reactions. Like cyclic guanidine derivatives, DBU can also be used as starting materials for the synthesis of ionic liquids. Moreover, as a precursor of synthetic ionic liquids, DBU has many advantages which are related to its properties, such as large size structure,

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strong charge delocalization, and low cationic symmetry.

It is well known that DBU has highly active nitrogen atoms in the heterocyclic skeleton, so that they can effectively undergo quaternization reaction and form nitrogen-containing heterocyclic ionic liquids with stable structures. In 2000, Kitazume et al. [2] reported the synthesis of two ionic liquids based on DBU and their use as reaction medium. Later Braun described the DBU ionic liquids in patent literature [3], and Tolstikova and Shainyan [4] published the synthesis of a series of DBU-based ionic liquids containing different substituents on the nitrogen atom.

Synthesis of DBU-Based Ionic Liquids

Synthesis of Protic DBU-Based Ionic Liquids

Neutralization of DBU with different Brønsted acids, including organic acids and inorganic acids, is a simple method to afford protic DBU-based ionic liquids (Scheme 2) [5–7].

The neutralization reaction between DBU and acids can be performed without using any solvent. And stoichiometric balance between the cation and the anion could be maintained by use of the definite mass of reagents with an exact equimolarratio of the acid and base. To avoid unexpected oxidation of the base, neat base was gradually added into acids under an N_2 atmosphere in a two- or three-neck round bottom flask kept in an ice-water mixture. After addition, the reaction

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DBU-Based Ionic Liquids, Scheme 1 Structure of DBU and the reaction with H₂O



DBU-Based Ionic Liquids, Scheme 2 Chemical structures of acids and protic DBU-based ionic liquids synthesis

mixture was stirred for several hours at room temperature. To ensure a complete neutralization reaction, a slight excess of amine was added, after which it was removed along with water by heating at 80 °C for 48 h under vacuum. Finally, the ionic liquid was dried under vacuum at 70 °C for 10 h.

The exception is the synthesis of [DBUH] $[(C_2F_5SO_2)_2N]$, which was prepared by a neutralization reaction of DBU with nitric acid to yield [DBUH][NO₃], followed by an anion exchange reaction with Li[$(C_2F_5SO_2)_2N$].

In addition to solvent-free synthesis, it can also be synthesized in methanol. For example, equimolar DBU and acetic acid or trifluoromethanesulfonic acid are directly neutralized in methanol. After reaction, the methanol was removed under vacuum. The crude IL was dried in vacuo at a constant temperature of 40 °C for overnight, then flushed with argon and stored in a glovebox [8].

DBU can also directly deprotonate some weak proton donors, such as fluorinated alcohols, imidazoles, pyrrolidinones, or phenols, to afford protic DBU ionic liquids. Scheme 3 shows some examples of anion functionalized ionic liquids, which were prepared through the neutralization reaction of DBU and imidazole, pyrazole, phenol, and 1,2,4-triazole, respectively [8–10].

The reaction of DBU with acid under conventional conditions usually takes a long time to complete (e.g., 48 h). Raval's group successfully synthesized [DBUH][CH₃CO₂] under ultrasound irradiation within 90 min [11]. In their experiment, aliquots of acetic acid (1 equiv.) were added over a period of 15 min to DBU (1 equiv.) by maintaining the temperature below 5 °C in an ice bath under ultrasound irradiation. Then the reaction mixture was exposed to ultrasound irradiation for an additional period of 15 min at ambient temperature. After the completion of reaction, obtained oily residue was dried in vacuum at 60 ° C for 1 h to afford [DBUH][CH₃CO₂] as a light yellow, viscous liquid.

Synthesis of Aprotic DBU-Based Ionic Liquids

Aprotic DBU-based ionic liquids mean that DBUbased ionic liquids were obtained by quaternization of the nitrogen atom with an alkyl chain or other group instead of a hydrogen atom. These DBUbased ionic liquids can be synthesized following a one/two-step protocol.

In 2000, Kitazume et al. [2] described the preparation of two DBU-based ionic liquids from direct alkylation of DBU with trifluoromethanesulfonic acid esters (Scheme 4). Specifically, into the precooled DBU, the same amount of ethyl trifluoromethanesulfonate or methyl trifluoromethanesulfonate was added slowly. After stirring for 2 h at room temperature, the mixture was heated at 70 ° C for 1 h to remove the volatile materials, giving [EtDBU][OTf] and [MeDBU][OTf].

Tolstikova and Shainyan [12] reported the synthesis of a series of ionic liquids containing different substituents on the nitrogen atom from DBU. Their methods include quaternization of DBU with alkyl halides or esters and anion exchange. The reaction of DBU with halohydrocarbons (Cl, Br, or I) can introduce substituents of varying carbon chain lengths or function groups on N atom to adjust properties of obtained ionic liquids [13– 15]. Moreover, by anion exchange, more types of ionic liquids based on DBU can be obtained. Since 2013, several research groups have reported the synthesis of DBU-derived ionic liquids. Although they are all quaternization and anion exchange processes, there are slight differences in the preparation conditions (Table 1). Post-treatment methods usually include filtration, washing, evaporation under reduced pressure to remove solvents, and purified with column chromatography.

Synthesis of DBU-Based Dicationic Ionic Liquids

In 2015, Sun et al. [20] reported the synthesis of a series of dicationic ionic liquids composed of bromine anion and different dications, including DBU-based dicationic ionic liquids (Scheme 5, right). The preparation procedure is as follows, DBU (2.1 equiv.) was dissolved in toluene at RT.

Then, 1, 4-dibromobutane (or 1, 2-dibromoethane, 1, 6-dibromohexane, 1 equiv.) was added slowly into the flask within 15 min in an ice bath and the reaction mixture was stirred at 80 °C for 12 h. An offwhite solid was formed after the solvent was remo ved by decanting. The solid product was washed repeatedly with ethyl acetate to remove nonionic residues and dried at 80 °C for 6 h under vacuum.

About 2 years later, Chu and Sun et al. [21] used a similar method to prepare DBU-based dicationic ionic liquid with chloride anion, and obtained other anionic ionic liquids through anion exchange (Scheme 5, left).

Characterization of DBU-Based Ionic Liquids

In general, the structure and composition of synthesized DBU-based ionic liquids need to be confirmed by means of NMR, IR, MS, etc. Moreover, these characterization techniques are also important tools for studying the interaction of ionic liquids with other substances.

NMR Characterization

NMR spectroscopy is an established technique for identifying organic compounds, and is therefore a natural avenue of investigation of ionic liquids.

For example, the ¹H NMR of [DBUH] $[CH_3CO_2]$ (Scheme 6) showed six different



DBU-Based Ionic Liquids, Scheme 3 Some DBU-based anion functionalized ionic liquid



DBU-Based Ionic Liquids, Scheme 4 Preparation of DBU-based ionic liquids containing CF₃SO₃⁻ anion

signals. The signal for three protons of CH₃ group appeared as a singlet at 1.766 δ value. The signal appeared at 1.517-1.675 & value as a multiplet was interpreted for six protons at position 3, 4, 5. The signal for two hydrogen at position 10 appeared at 1.842–1.901 δ value as a multiplet. The signal appeared at 2.394–2.650 δ value as a multiplet was interpreted for two protons at position 6. The two protons attached to ring carbon having nitrogen atom on one side (at position 2) appeared as a multiplet at slightly downfield region of the spectrum, that is, 3.165-3.193 δ . Similarly the four protons at position 9 and 11 appeared as a multiplet at 3.278–3.437 δ . ¹³C NMR spectrum showed nine signals in aliphatic region at 19.5–54.1 δ . Two signals at 165.9 δ and 179.4 δ stand for the carbon at position 7 and carbonyl carbon, respectively, present in the structure.

Take [C₆DBU][SCN] [22] as an aprotic DBUbased ionic liquid example, its structure was identified by NMR. Based on the ¹H NMR chemical shift, the value at $\delta = 0.87$ ppm corresponds to the three hydrogen atom on C17. At $\delta = 1.30$ ppm, the six hydrogen atoms correspond to the protons on carbon atoms at C7, C8, C16. The two hydrogen at multiplet $\delta = 1.54$ ppm correspond to the protons on carbon atoms at C4. The multiplet at $\delta = 1.67$ ppm corresponds to six hydrogen atoms at C6, C14, and C15. The two multiplet at $\delta = 1.97$ ppm correspond to hydrogen atoms at C3. Another multiplet at $\delta = 2.86$ ppm represents proton on C9 carbon atom. The multiplet at $\delta = 3.36$ ppm is related to the two hydrogen on

		D.C
Structure	Preparation conditions	Ref.
	n = 4, 6, 8; X = Cl	[14]
	DBU:RCl =1:1.2; 50 °C 48 h under agitation, without solvent	
	n = 12, 14, 16; X = Br	[13]
$ \langle [] \oplus] ^{\times}$	DBU:RBr = 1:1.1; toluene refluxed 24 h	
	n = 1, 3, 5, 7, 9, 13; X = Cl/Br	[15]
[CnDBU][X]	DBU: RX = 1:1.2; MeCN, 60 °C, 48 h	
	1) quaternization	[16]
	$n = 0, 1; X = I, NTf_2, B(CN)_4$	
	DBU: RI = 1:1.6; AcOEt, rt., 24 h	
	2) anion exchange	
	LiNTf ₂ (1.1 equiv.), H ₂ O, rt., 24 h	
	KB(CN) ₄ (1 equiv.), MeOH, rt., N ₂ , 24 h	
с л	1) quaternization	[17]
R	R-X: Alkyl halides or acid halides of different chain lengths (C^2-C^{16}) , X = Cl or Br	
	DBU: $R-X = 1:1.01$; 120–125 °C, without solvent	
⟨	2) anion exchange	
	KF (1.5–3.0 equiv.), rt., $H_2O/MeOH$ (1:9)	
[RDBU][F]		
	1) quaternization	[18]
[_R][o [⊖]]	R-X: Bromoethane, allyl bromide, butyl bromide, benzyl chloride	
	DBU:R-X = 1:1.6; AcOEt, rt., 48 h	
	2) anion exchange	
	Potassium benzene sulfonate (1.16 equiv.), MeCN, rt., 48 h	
R-DBUBS		
	n = 1, 3, 5, 7, 9, 13;	[15]
\times^{CH_3}	[C _n DBU][X] with NaSCN (1.5 equiv.), DCM, rt., 24 h	
SCN [⊕]		
[CnDBU][SCN]		
	$n = 1, 2, 3; G = CH_3 \text{ or } OH, X = Br$	[19]
$\begin{bmatrix} \cdot \times^{G} \end{bmatrix}$	DBU:RBr = 1:1; AcOEt, refluxed, 2 h	
	n = 3; G = CH ₃ , X = Im	[9]
	1) guaternization	1.1
	R-X: Bromoethane, allyl bromide, butyl bromide, benzyl chloride DBU:	
	$C_4H_9Br = 1:1.6$; AcOEt, rt., 48 h	
	2) anion exchange	1
	Anion-exchange resin (OH ⁻)	
	3) neutralization	
	Imidazole (1 equiv.), water, rt., 24 h	

DBU-Based Ionic Liquids, Table 1	Representative examples of DBU-based	d ionic liquids synthesis procedures
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C13 while multiplet at $\delta = 3.45$ represents the hydrogen at C2 and C10, respectively. The multiplet at $\delta = 3.63$ ppm represents the two hydrogen at C12.

In addition to characterizing the structure of ionic liquids, NMR technology is also used to study the influence of environment on the microscopic structure of DBU-based ionic liquids in solutions of organic solvents, as well as to study the reaction mechanism catalyzed by these ionic liquids.

Very recently, Dai et al. [23] studied the interactions between [DBUH][Im] and organic solvents through ¹H NMR chemical shifts of -NH in [DBUH][Im] at different concentrations based on local composition model, in order to uncover



DBU-Based Ionic Liquids, Scheme 5 Synthesis of DBU-based dicationic ionic liquids



DBU-Based Ionic Liquids, Scheme 6 Structures of [DBUH][CH₃CO₂] and [C₆DBU][SCN]

the microscopic structures of [DBUH][Im] in mixtures. Figure 1 is the ¹H NMR spectra of all binary solution, which clearly shows the change in -NH chemical shift with concentration. The ¹H NMR spectra were obtained using a Bruker AV 400 spectrometer operating at 400 MHz at different concentrations at 298.15 K.

Gao's group studied the reaction mechanism of CO₂, epoxides, and amines catalyzed by DBU-[DBUH][Br] using NMR technology combined with DFT calculation [24]. ¹H and ¹³C NMR spectroscopy were used to investigate the interactions between the catalysts and the substrates. They observed that the resonance of the N-H¹ proton of [DBUH][Br] shifted downfield from

 $\delta = 10.005$ to 10.019 ppm upon the addition of 1 equivalent of ethylene oxide (EO). This phenomenon indicates an interaction between [DBUH][Br] and EO, that is, a hydrogen bond is formed. So, [DBUH][Br] acts as a hydrogen bond donor to activate EO. Because the upfield shift of the resonance of C¹ of EO (from $\delta = 39.86$ to 39.53 ppm) was exactly the opposite of that reported in the literature, the authors believed that in addition to hydrogen bond interaction, Br⁻ also interacted with the carbon atom of EO, which increased the electron density around the carbon atom to result in the upfield shift of the resonance of C¹ (Scheme 7). On the other hand, the changes of ¹H NMR spectra concerning with

DBU-Based Ionic Liquids,

Fig. 1 ¹H NMR spectra of [DBUH][Im](1)/DMSO(2) (top), [DBUH][Im](1)/ DMF(2) (middle), and [DBUH][Im](1)/ethanol(2) (bottom) systems at different concentrations (Copyright from Elsevier)

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DBU mixed with aniline or 2-(phenylamino)ethanol demonstrated that DBU could activate the hydroxyl group and NH group of 2-(phenylamino)ethanol through hydrogen bonds, especially on the hydroxyl group.

Watanabe et al. have evaluated the relationship between the ¹H chemical shifts of the N-H protons in protic DBU-based ionic liquids and the ΔpK_a values of the constituent acids and bases of the ionic liquids and found a linearly correlation between the two. Moreover, the ¹H chemical shift of pure DBU and protic [DBU]-based ionic liquids indicated that only the imino-nitrogen accepts protons during neutralization, even though DBU contains both imino and amino nitrogens, which agrees with the results of previously conducted studies [5].

Thermal Analysis

Compared with conventional organic solvents, ionic liquids have high thermal stability, and of course, they are much higher than the thermal stability of synthetic ionic liquid raw materials. The thermal stability of DBU-based ionic liquids is a unique property that determines their applicability in a number of industrial processes. Hameed et al. [17] investigated the stability of DBU-based fluorinated ionic liquids in comparison to TBAF (tetra butyl ammonium fluoride) via binding energy calculations based on DFT method. From the binding energy data, it is obvious that all DBU-ionic liquids have much lower bonding energy values than that of TBAF, which means a much stable structure.

Dai's group also proved that DBU-based ionic liquids have high thermal stability via thermogravimetric analysis [16]. They studied the thermal decomposition temperature of alkylsubstituted DBU ionic liquids with anions Tf_2N and $B(CN)_4$. It was found that decomposition temperatures of $[C_1DBU][Tf_2N]$ (420.5 °C), $[C_1DBU][B(CN)_4]$ (409.4 °C), $[C_2DBU][Tf_2N]$ (418.5 °C), and $[C_2DBU][B(CN)_4]$ (419.5 °C) are much higher than many ammonium and imidazolium ionic liquids. However, similar DBU-based thiocyanate and dicyanamide ionic liquids show slightly lower decomposition temperature near 350 °C.

Generally, the thermal stability of protic ionic liquids is low because of the possibility of a reverse reaction to produce free acids and bases. Watanabe et al. prepared a series of protic ionic liquids through neutralization of DBU with different Brønsted acids, and studied the correlation between ΔpK_a of the constituent amine and acids with thermal stabilities. The results of the thermogravimetric analyses indicate that protic DBU-based ionic liquids with $\Delta pKa \ge 15$ exhibit excellent thermal stability similar to aprotic ionic liquids with $\Delta pKa \ge 20$ show remarkably high short-term thermal stability up to ca. 450 °C under a nitrogen atmosphere [5].

FT-IR Characterization

FTIR spectroscopy is an effective analytical method for detecting functional groups and characterizing covalent bonding information. As for protic DBUbased ionic liquids, the adsorption bands in the ranges of 1500–1800 and 2900–3350 cm⁻¹ confirmed the characteristic peak of N-H bending and stretching modes, respectively.

Generally speaking, a distinctive feature that helps identify the cation of DBU-based ionic liquid are the set of bands representing the N,N-disubstituted amidine. For instance, from FTIR spectra of $[C_1DBU][Tf_2N]$, $[C_1DBU][B$ (CN)₄], $[C_2DBU][Tf_2N]$, and $[C_2DBU][B(CN)_4]$, it is obvious that the first band corresponding to the imine C=N stretch in the amidine appears with strong intensity near 1630 cm⁻¹. The second band of a medium intensity peak located from 1550 to 1530 cm⁻¹ with variability in position depending on the bicyclic structure and substituent. Also, the peaks in the range of ~2850–3000 cm⁻¹ represent CH stretching modes which allows for another characteristic fingerprint of the cation [16].

For B(CN)₄ anion, the presence of a small peak near 2218 cm⁻¹ is indicative of the nitrile CN asymmetric stretch. There is also a strong peak around 927 cm⁻¹ which shows the B-C stretching. As for those with the bis(trifluoromethanesulfonyl) imide anion, the peaks around 1053, 1134, 1176, and 739/788 cm⁻¹ are in agreement with those attributed to the cis/trans conformers of [Tf₂N].

Cross-References

- Bronsted acid ionic liquids: not only simple acid catalysts or solvents
- Chemical Reactions in ionic liquids
- Immobilization of Ionic Liquids, Types of Materials, and Applications
- Task-Specific Ionic Liquids: Design, Properties and Applications
- Thermal Stability of Ionic Liquids

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