Reversible Task-Specific Ionic Liquids From Chiral Pool Using CO_2 And Organic Superbases

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ABSTRACT

From a set of amino-acids, carbamate based ionic liquids and molten salts were prepared in a single step using CO_2 and two organic superbases (DBU or TMG). L-Valine carbamate based salts were selected as model compounds to discuss further. The obtained salts were characterized by ^{1}H-RMN, ^{13}C-RMN, FTIR, solubility profiles and DSC thermal analysis as well. The superbases tested play a fundamental role in the solubility and thermal profile of the L-valine carbamate-based salts. The DBU derived compound is soluble in water, DMSO and Acetonitrile, while similar TMG salt is only soluble in water and DMSO. The thermal studies indicate us that the prepared TMG derived carbamate salt of L-valine decomposes (CO_2 loss) at considerable higher temperatures than equivalent DBU based salt.

INTRODUCTION

The concept of CO_2 capture and utilization for the production of added-value compounds [1] is attractive nevertheless issues such as poor reactivity of CO_2 need to be solved in a sustainable framework. It's well documented in the literature that CO_2 reacts with nucleophiles such as amines [2,3] or alcohols, [4] leading to carbamate and carbonate derivatives, respectively. Based on such reactivity profile, different chemical systems were designed with many potential applications, specifically, reversible ionic liquids [2-4], to be used as system with switchable polarity and volatility in reactions and/or extractions [5], systems for CO_2 capture [6, 7] or even manipulation of fluorescence quench [8]. Based on the combination of a nucleophile (alcohol), an organic superbase and CO_2, Jessop et. al. [4], created the concept of reversible ionic liquid based on CO_2. Later on, other aspects of this paradigm were explored such as usage of other gases (SO_2, COS, CS_2) as elements of reversibility [9], different nucleophiles, like amines [2, 3], amino-alcohols [10] and amino-esters [11], or even the type of superbase and the number of functionalities present in the same molecule able to react as nucleophiles [2]. In parallel, different systems for chemical CO_2 capture are described in the literature. Among them is the more traditional method applied in industry for more than 60 years, the use of aqueous solutions of alkanolamine. Such method has intrinsic drawbacks: solvent loss, degradation and high energy demand [12]. Other alternatives emerged with the advent of ionic liquids, and specifically, task-specific ionic liquids that, combining the low volatility and wide liquid range with specific functionalities, were able to efficiently capture CO_2 [6, 7, 13-16]. The high price and number of synthetic steps required to prepare this task-specific ionic liquids are the major obstacles for implementation at large scale. The work here presented is based on the concept of

reversible ionic liquids, using CO_2 as element of reversibility, low-cost organic superbases and a generic aminoacid from chiral pool as nucleophile.

MATERIALS AND METHODS

L-Valine was supplied by Alfa Aesar with a purity of 99%. 1,1,3,3 tetramethylguanidine (TMG), 99%, was supplied by Sigma-Aldrich (water removed using molecular sieves), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), $\geq$ 99%, was provided by Fluka (with water removed using molecular sieves) and dichloromethane, p.a. grade, supplied by Sigma-Aldrich. 99,998 mol% carbon dioxide was supplied by Air Liquide.

The syntheses were performed in a cylindrical high pressure steel reactor (11 mL) with sapphire windows at both ends.

In a generic reaction, 2 equivalents of superbase dissolved in dichloromethane were added to 1 equivalent of L-valine suspended in the same solvent. CO_2 was introduced to the resultant reaction mixture until a pressure of 20 bar was reached. The reactions were performed at room temperature and the mixture between elements of reaction was promoted using magnetic stirrer during the period of reaction (8-9 hours). After that period, the solvent was removed by *in situ* continuous stream of CO_2 during 2 hours at room temperature. The resultant product was stored at a temperature of approximately 7ºC.

The obtained compounds were characterized ^{1}H and ^{13}C NMR recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million from a tetramethylsilane reference. IR spectra were recorded on a Perkin Elmer FTIR Spectrometer, Spectrum 1000 and Spectrometer FTIR Bruker Tensor 27. The samples were prepared in a KBr matrix. DSC analysis was carried out using a TA Instruments Qseries TM Q200 DSC with a refrigerated cooling system. The solubility in reference solvents was obtained using the following method: solvent was added, drop by drop, to a weighted sample of each compounds prepared in this work until a homogeneous solution arises. The resulting saturated mixture was weighted and the solubility calculated.

RESULTS

Starting from a set o amino-acids (Glycine, L-Alanine, L-Valine, L-Leucine, L-Phenylalanine, DL-Tryptophan) in combination with two organic superbases (DBU and TMG), a series of carbamate based salts were prepared using CO_2 as element of functionalization. In order to illustrate the concept L-Valine was selected as model aminoacid (Figure 1) for discussion of results.

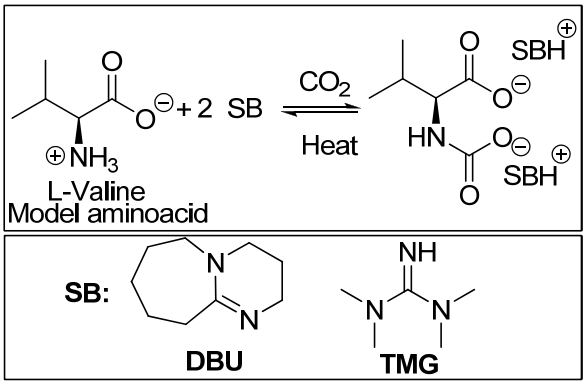
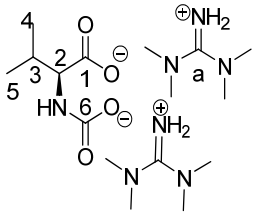
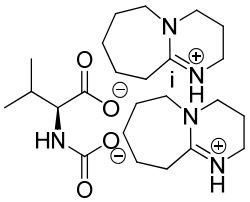


Figure 1: The concept of reversible ionic liquid using CO_2 as element of reversibility, an amino-acid (L-Valine) and an organic superbase (DBU or TMG).

According ^{1}H-NMR spectra there's a clear indication in both L-Valine based salts prepared that the ratio cation:dianion is 1:2 as expected. In order to check if the carbamate functionalization using CO_2 occurred, some ^{1}H and ^{13}C-NMR peaks and FTIR bands arisen as markers (Table 1). Comparing the ^{1}H-NMR spectra of L-Valine and the respective carbamate based salts, it is possible to verify a significant difference in the chemical shifts of proton H-2 (Table 1), as this proton becomes more de-shielded in the prepared salts (3.23 and 3.28 ppm vs 2.98 ppm in L-Valine in the same deuterated solvent - DMSO). In order to contextualize this result, it is important to highlight that ^{1}H-NMR simulations indicate that chemical shift of H-2 follows the order: dianionic carbamate-functionalized L-Valine > zwitterionic L-Valine > anionic L-Valine. According these observations it is possible to conclude that the carbamate based desired products were obtained in both cases. Considering ^{13}C-NMR spectra of TMG based salt is possible to observe two peaks (174.18 and 174.20 ppm) corresponding to carboxylate and carbamate carbons. The same spectrum is indicative of protonated TMG (162.88 ppm) by comparison with a previous work performed in our group [17]. Moreover, FTIR spectra show characteristic bands for the carbamate functionality at 1700 cm^{-1} (slightly shifted when compared with Bates et al. [7]), 1567 cm^{-1}, (according Yamada and collaborators [11). Three more carbamate characteristic bands (1398, 1008 and 831 cm^{-1}) that were revealed by comparison with the spectra of ammonium carbamate and ammonium chloride available in SDBS spectral database [18]. Similarly the same characteristic carbamate FTIR bands were found in the DBU based salt (Table 1). Curiously the DBU based salt presents two sets of four peaks each, in the zone corresponding to carbamate and carboxilate in the ^{13}C-NMR spectra, indicative that probably there are no free rotation around carbamate and/or carboxilate functionalities related with the considerable size of $DBUH^{+}$ and isopropyl side-chain of L-Valine moiety. Regarding C-i, the respective chemical shift (164.29 ppm - Table 1) is indicative of protonated DBU [17].

Table 1: Spectral profile of the model carbamate based compounds

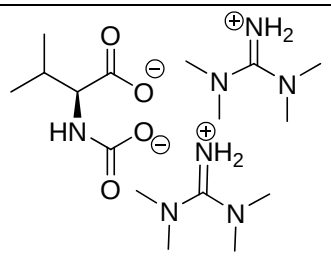
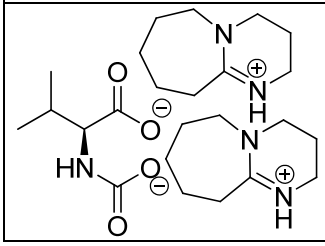
	^{1}H-NMR H-2 L-Valine (DMSO) ppm	^{1}H-NMR H-2 (DMSO) ppm	^{13}C-NMR C-1, C-6 (DMSO) ppm	^{13}C-NMR (C-a, C-i) (DMSO) ppm	FTIR (KBr) Carbamate characteristic Bands cm^{-1}
	2.98	3.23	174.18 and 174.20	(162.88, -)	1700 (m), 1567 (s), 1398 (m), 1008 (w), 831 (w)
		3.28	(175.20, 175.21 175.22, 175.23) and (175.28, 175.30, 175.31, 175.33) (Different conformers	(-, 164.29)	1700 (m), 1583 (s), 1398 (m), 1009, (w), 831 (w)

As to the physico-chemical properties (Table 2), both prepared model salts have a melting point below 100ºC, which makes them ionic liquids by definition. The fact that the difference in melting points between the two model compounds is very small is indicative that this property is not very sensitive to the type of superbase tested. Probably the observed difference is due the conformational constraints observed for the DBU-based salt (Table 1), which are not observed in the TMG based equivalent.

On the contrary, the decomposition temperatures (T_d), associated with loss of CO_2 from the carbamate functionality, show a significant difference. The TMG based compound has T_d > 120ºC, probably due to a stabilization of the carbamate functionality by a six-ring hydrogen bond interaction with $TMGH^+$ (Figure 2), similarly to what was reported previously by Heldbrandt et al [19] for the carbonate functionality. In the DBU-based salt, such stabilization is not possible and the value of T_d is significantly lower (96ºC).

As to the solubility profiles of the studied compounds,besides water, they are also soluble in DMSO, with DBU-based compound also soluble in acetonitrile. This observation is indicative of a potential to process amino-acids in organic solvents and particularly in volatile acetonitrile.

Table 2: melting points, decomposition temperatures of carbamates and solubilities in reference solvents

	mp (ºC)	**T_d** (ºC)	**Solubilities** **mg/g (solvent)**				
			H_2O	ACN	DMSO	DCM	Acetone
	82	> 120	213	< 8	319	< 2	< 10
	89	96	158	66	172	< 3	< 19

ACN: acetonitrile and DCM: dichloromethane.

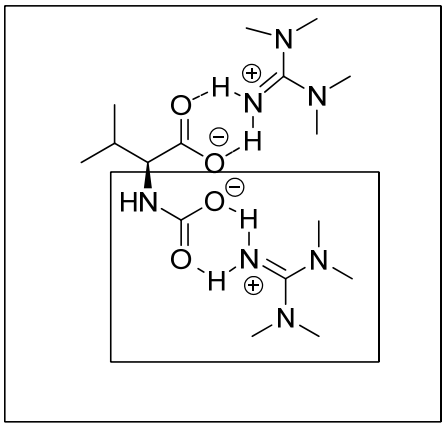


Figure 2: Effect of stabilization of the carbamate functionality based on six-ring hydrogen bond interaction with $TMGH^+$.

CONCLUSION

A novel methodology for functionalization of amino-acids from chiral pool in the presence of CO_2 and organic superbases was developed with carbamate functionality obtained during reaction as proof by several spectroscopic techniques. The prepared model compounds based on L-Valine present different properties such as higher temperature required for CO_2 release from carbamate of $TMGH^+$ based compound associated to a stabilization by six-ring hydrogen bond interactions between carbamate and $TMGH^+$. Besides water, both model compounds are soluble in DMSO while DBU based compound is also soluble in Acetonitrile.

The prepared compounds and associated methodology have potential application as cheap reversible system for CO_2 capture and release, reversible manipulation of solubilities of natural compounds, *in situ* manipulation of enantiomeric-dependent characteristics of chemical systems such as basic catalysis, and protection of amine group of amino-acids.

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