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Carbon dioxide utilization in the efficient synthesis of carbamates by deep eutectic solvents (DES) as green and attractive solvent/catalyst systems

A green and eco-friendly solvent/catalyst system based on deep eutectic solvent (DES) was devised and developed for the simple synthesis of carbamates through three-component coupling of amines, alkyl halides and carbon dioxide (CO₂). It was found that choline chloride:Zinc (II) chloride ([ChCI][ZnCl₂]₂) was very proficient and effective for the activation and utilization of CO₂ in carbamate formation reactions from the wide scope of amines. Surprisingly, this strategy provides the desired carbamates under atmospheric CO₂ pressure in room temperature. Particularly, both aromatic and aliphatic amines were so effective and demonstrated excellent yields. Besides, the [ChCI][ZnCl₂]₂ exhibited very high stability and also could be reused at least for over five consecutive cycles without any significant loss of activity. It is worth noting that

this is the first solvent/catalyst system which can be recycled successfully from the reaction mixture.

Introduction

The development of green and eco-friendly processes is an important challenge in industrial organic chemistry and has received many attentions in recent years.¹ One of the most promising processes in the ecological and economic points of view is the direct synthesis of the useful and high-value organic compounds such as carbamates by using carbon dioxide (CO_2) as a safe, nonflammable, low-cost and abundant renewable carbon source.² However, the high inherent thermodynamic stability of this molecule is the main obstacle of its efficient application in organic reactions.³ Nevertheless, numerous organic compounds including carbonates, urea derivatives, carboxylic acids, alcohols, carbamates and polymers have been directly synthesized from CO₂.²⁻⁴ In this context, the elaborate design and development of an efficacious method for the synthesis of carbamate derivatives are one of the attractive and exciting synthetic goals because of their wide applications in medicines, agrochemicals and dyes.⁵ Moreover, they can also be used as protecting groups and versatile intermediates for the various synthetic applications.⁶

As the industrial method, carbamates are conventionally prepared from phosgene or its derivatives (Scheme 1 A).⁷ In the green and safety points of view, the major environmental problems of these methods are the high toxicity of phosgene and production of corrosive salts as the main by-product. Besides the health and environmental risks associated with the use of phosgene and its derivatives, there are also major

concerns attributed to their production and storage.⁸ Therefore, a lot of efforts have been devoted to explore and develop green alternative methods utilizing other carbonyl sources (Scheme 1 B).⁹ Although many phosgene-free processes for the synthesis of these compounds have been reported, most of these methodologies suffer from some serious drawbacks like harsh reaction conditions, additional reagents that generate lots of wastes and exhibit poor functional group tolerance.⁹⁻¹⁰

A) Classic method

$$R^{1}-NH_{2} + X \stackrel{I}{\xrightarrow{}} X + R^{2}-OH \longrightarrow \stackrel{I}{\xrightarrow{}} R^{1} \stackrel{I}{\xrightarrow{}} R^{2} \stackrel{I}{\xrightarrow{}} R^{2}$$

B) Phosgene-free methodes

X= Cl. CCk. Im. Bt



C) This work:



Scheme 1. Different carbonyl sources used for the synthesis of N-substituted carbamates.

Nowadays, the conversion of amines to carbamates by using CO_2 as the carbon source is one of the most suitable and attractive routes which have been investigated so far.¹¹⁻²⁰

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59 60 Generally, a few routes have been developed for this transformation including the reaction of amines and carbon dioxide with a different third component such as alcohols,¹² metal alkoxide,¹³ epoxides,¹⁴ alkoxysilanes,¹⁵ tosylhydrazones, ¹⁶ diaryliodonium salts,¹⁷ aryloxyallenes,¹⁸ arylboronic acids¹⁹ or alkyl halides.²⁰⁻²³ During the past two decades, considerable academic and industrial efforts have been devoted to the development of efficient catalytic systems for this transformation. However, most of these methods suffer from some limitations such as long reaction times, high pressure of CO2, tedious workup and low yields specifically for the carbamates obtained from aromatic amines.¹¹⁻²⁰ Compared to these approaches, carbamate synthesis from CO₂, amines and alkyl halides would be ideal and effective because all substrates are easily prepared with high yields under atmospheric CO₂ pressure. Although, numerous catalyst systems including base catalysts (Cs₂CO₃, K₂CO₃ and DBU),²¹ onium salts catalysts (Bu₄NBr, KO₂/ Bu₄NBr, triton-B)²² and metal catalysts (Ir, Pd and Zn)²³ have been developed for this transformation, most of which are homogeneous catalysts and suffer from laborious purification processes. In addition, these catalysts cannot be recovered and reused from the reaction. Nevertheless, the development and exploration of green, sustainable, recyclable and highly efficient catalysts still need to be fulfilled.²⁰⁻²³

The excessive use of organic solvents especially halogenated solvents in various industries is one of the most important factors in the pollution of the environment. In fact, they show many intrinsic drawbacks such as flammability, high toxicity, non-biodegradability and accumulation in the atmosphere (low boiling points).²⁴ Therefore, new alternatives have been investigated to avoid more environmental pollution.²⁵

Deep eutectic solvents (DESs) represent an alternative class of room temperature ionic liquids (RTILs) which have attracted the attention of many scientists in recent years.²⁶ Indeed, to overcome the limitations of ILs such as toxicity, poor biodegradability and high cost that have highlighted in some studies, a new type of green solvents called DESs have emerged.^[26] Furthermore, the DESs have a lot of advantages like easy preparation, high purity, low cost, no interaction with water, poor conduction, high viscosity, low vapor pressure, high thermal stability, non-toxicity, reusability and biodegradability.²⁶⁻²⁸ Furthermore, they can be applied in many reactions as a catalytic active species and also as the reaction medium. Consequently, the application and efficiency of DESs as the green and eco-friendly catalyst, solvent or co-solvent in the synthesis of many compounds are very considerable and undeniable.28

Our research group has been engaged during the past several years to develop new, effective and eco-friendly methodologies for the phosgene-free synthesis of carbamates, thiocarbamates, dithiocarbamates and ureas.²⁹ Very recently, we have reported an efficient and mild synthesis of variety carbamates from urea as a safe and green carbonyl source.^[30] As a part of these efforts, we herein demonstrated an effective and general one-pot method for the synthesis of organic

carbamates by a three-component coupling reaction of CO₂, amines, and alkyl halides in the presence of choline chloride:Zinc (II) chloride ([ChCl][ZnCl₂]₂) as a recoverable catalyst and reaction media under the mild conditions (Scheme 1 C).

Results and discussion

At the outset of our study, we examined different reaction parameters including the type and amount of DESs, the molar ratios of reagents, temperature and reaction time in the formation of carbamates for exploring the optimal reaction conditions. For this purpose, the reaction of aniline and 1-bromopropane under 1 atm CO_2 pressure was selected as the model reaction and the results are presented in Table 1.

Table 1. Optimization of reaction parameters for one-pot synthesis of 1-propyl phenylcarbamate (C1) under 1 bar CO₂ pressure.

() + `	Br [ChCl][ZnCb]2		_ا ╨_∽	\checkmark	
A1 E		B1	C1			
Entry	Molar rati A1:B1[mmo	o DES	DES [mmol]	Temp [°C]	Tim [h]	Yield (%) ^a
1	1:1.2	[ChCl][LaCl ₃] ₂	10	R.T	2	68
2	1:1.2	[ChCl][CrCl ₃] ₂	10	R.T	2	49
3	1:1.2	[ChCl][CoCl ₃] ₂	10	R.T	2	31
4	1:1.2	[ChCl][NiCl ₂] ₂	10	R.T	2	34
5	1:1.2	[ChCl][CuCl ₂] ₂	10	R.T	2	17
6	1:1.2	[ChCl][FeCl ₃] ₂	10	R.T	2	19
7	1:1.2	[ChCl][CsCl] ₂	10	R.T	2	57
8	1:1.2	[ChCl][CeCl ₃] ₂	10	R.T	2	61
9	1:1.2	[ChCl][SnCl ₂] ₂	10	R.T	2	66
10	1:1.2	[ChCl][ZnCl ₂][SnCl ₂]	10	R.T	2	79
11	1:1.2	[ChCl][ZnCl ₂] ₂	10	R.T	2	95
12	1:1.2	[ChCl][ZnCl ₂]	10	R.T	2	87
13	1:1.2	$[ChCl][ZnCl_2]_{1.5}$	10	R.T	2	90
14	1:1.2	[ChCl][ZnCl ₂] ₃	10	R.T	2	94
15	1:1.2	none	0	R.T	24	0
16	1:1.2	[ChCl][ZnCl ₂] ₂	6	R.T	2	81
17	1:1.2	[ChCl][ZnCl ₂] ₂	14	R.T	2	95
18	1:1.2	[ChCl][ZnCl ₂] ₂	20	R.T	2	94
19	1:1	[ChCl][ZnCl ₂] ₂	10	R.T	2	86
20	1:1.1	[ChCl][ZnCl ₂] ₂	10	R.T	2	91
21	1:1.3	[ChCl][ZnCl ₂] ₂	10	R.T	2	95
22	1:1.4	[ChCl][ZnCl ₂] ₂	10	R.T	2	95
23	1:1.2	[ChCl][ZnCl ₂] ₂	10	50	2	90
24	1:1.2	[ChCl][ZnCl ₂] ₂	10	70	2	83
25	1:1.2	[ChCl][ZnCl ₂] ₂	10	R.T	1	67
26	1:1.2	[ChCl][ZnCl ₂] ₂	10	R.T	1.5	78
27	1:1.2	[ChCl][ZnCl ₂] ₂	10	R.T	3	94
28	1:1.2	[ChCl][ZnCl ₂] ₂	10	R.T	5	95

^a Isolated yield.

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In the first step, the efficiency of the model reaction have been investigated in the presence of wide range of attractive DESs which are easily prepare from ChCl and the metal halides such as LaCl₃, CrCl₃, CoCl₃, NiCl₂, CuCl₂, FeCl₃, CsCl, CeCl₃, SnCl₂ and ZnCl₂ (Table 1, entries 1-14). It is observable that the DES of choline chloride and Zinc (II) chloride ([ChCl][ZnCl₂]₂) gave the best yields (Table 1, entry 11). Additionally, the result showed that the usage of choline chloride and Zinc (II) chloride in the other molar ratios (1:1, 1:1.5 and 1:3) in the model reaction did not present better yields may be due to the different viscosity of them (Table 1, entries 12-14). Subsequently, the effect of the presence of [ChCl][ZnCl₂]₂ as a solvent/catalyst system in different amounts was explored (Table 1, entries 15-18). As expected, no desired product was detected in the absence of [ChCl][ZnCl₂]₂ even after 24 hours (Table 1, entry 15). It was obviously shown that the presence of [ChCl][ZnCl₂]₂ as a solvent/catalyst system is necessary for obtaining the desired carbamate. The maximum yield was observed when the 10 mmol (5 cm^3) of DES was used (Table 1, entry 11). Furthermore, the effects of various molar ratios of aniline and 1-bromopropane in the model reaction were investigated and the best result obtained when the molar ratio of 1:1.2 for aniline: 1-bromopropane was applied in this reaction (Table 1, entries 19-22). Moreover, we found that the yield and selectivity of the model reaction were strongly affected by the reaction temperature (Table 1, entries 23-24). In fact, the yield and selectivity of this reaction decreased with an enhancement in reaction temperature up to 70 $^{\circ}$ C because of the formation of urea as a by-product. Finally, the reaction time was investigated (Table 1, entries 25-28).

The best catalytic system and optimal reaction conditions were identified. Next, we sought to investigate the performance and limitation of this methodology in more detail. Due to this fact that carbamates are usually used as intermediates to protect the functionality of amines in the multistep organic synthesis, the generality and ability of this method were firstly tested considering the use of various amines. To that purpose, a set of primary and secondary amines including aromatic, heteroaromatic, alicyclic, and aliphatic were reacted with1-halopropane under the optimal reaction conditions (Table 2).

It was found that the anilines bearing the electronwithdrawing groups as well as the electron-donating groups took part in the reaction very well and provided the desired product in excellent yields (Table 2, entries 1-13). It should be noted that halide substituted anilines were well tolerated and provided the corresponding products, while no side-products were obtained at all (Table 2, entries 9-10). Moreover, thiophen-3-amine as a heterocyclic amine source has promising tolerance against the reaction conditions and prepared the desired carbamate in very satisfactory yield (Table 2, entry14). As it can be seenin Table 2, the aliphatic amines are better nucleophiles than aromatic amines. Aliphatic amines were very effective substrates for these reactions and the desired carbamates were obtained in excellent yields (Table 2, entries 15-18).



X= Br, 95 %^b

X= Cl, 90 %^b

X= Br, 97 %^b

X= Cl, 92 %^b

X= Br, 96 %^b

X= Cl, 90 %^b

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^a Reaction conditions: amine (1 mmol), 1-halopropane (1.2 mmol), CO_2 pressure (1 atm), [ChCl][ZnCl₂]₂ (10 mmol/5 cm³), room temperature, 2 h. ^b Isolated yield.

The reaction was also performed very well with the secondary aliphatic and aromatic amines but in a somehow lower yields in comparison with primary aliphatic amines and anilines (Table 2, entries 19-24). More likely, the reason for this decrease in efficiency is the increase in the effect of steric hindrance. The obtained results notably showed that alkyl chlorides like alkyl bromides, gave great performance in the synthesis of carbamates with this method however with a little lower yields than aryl bromides.

After the extremely interesting results that were obtained for the investigation of various amines and anilines in the synthesis of carbamates using CO_2 , we decided to go on with focusing on the application of various alkyl/aryl halides in these reaction conditions. Therefore, to show the synthetic utility of this method, a variety of alkyl, allyl and benzyl halides groups were subjected to the optimized conditions.

A variety of primary, secondary and tertiary alkyl halides (bromide and chloride) were examined in this reaction and interestinglythey all were proved to be applied very well (Table 3, entries 25-33). Additionally, allyl and benzyl halides can efficiently generate the corresponding carbamates in excellent yields (Table 3, entries 34-36). It should be noted that all of our efforts for preparing the carbamates with aryl halides in these reaction conditions were unsuccessful.

Details of the reaction mechanism are not identified completely at this moment and the novelty and complexity of this catalytic system emphasizes that further investigation is needed. Nevertheless, the possible mechanism is proposed as shown in Scheme 2. According to the information in the literature,³¹ the OH groups of choline chloride are capable of reacting with CO₂ to form the alkyl carbonate salt under ambient conditions. finally, the carbonyl group of dialkyl carbonate is activated by the [ChCl][ZnCl2]₂ and then get attackedby amine or aniline, and the carbamate derivatives are produced as the final products.At the same time, [ChCl][ZnCl2]₂ is regenerated to complete the catalytic reaction cycle.

 Table 3. Comparison of the alkyl halides activity in the synthesis of carbamates.^a







Scheme 2. The proposed mechanism.

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In general, the recovery and reusing of a catalyst reduces the overall process cost and destructive effects on the environment. The application of recyclable catalysts has a great impact on their exploitation in the industrial processes both from economic and environmental points of view. Therefore, the recyclability of [ChCl][ZnCl₂]₂ as a solvent/catalyst system in the model reaction was investigated. In the recycling experiment of [ChCl][ZnCl₂]₂ after each round, all products and remaining precursors were extracted with diethyl ether after performing the model reaction. Then, the [ChCl][ZnCl₂]₂ was simply recovered by biphasic extraction with ethyl acetate. After drying the [ChCl][ZnCl₂]₂ by evaporation at 70 ^oC under vacuum condition for 30 min, the recovered [ChCl][ZnCl₂]₂ was reused for the next runs of model reaction. As illustrated in Figure 1, only a slight decrease in the catalytic activity of recovered [ChCl][ZnCl₂]₂ in the model reaction was observed after five successive cycles.



Figure 1. Recycle and reuse of $[ChCl][ZnCl_2]_2$ in the carbamate synthesis.

Conclusions

In this work, the development of an innovative, ecofriendly and effective strategy to produce carbamates through three-component coupling of amines, alkyl halides and carbon dioxide (CO₂) under mild conditions is reported. More attractively, the ability of eutectic solvent ([ChCl][ZnCl₂]₂) as an eco-friendly solvent/catalyst system with high efficiency greatly provides more economical and green conditions in addition to its good catalytic potency. The [ChCl][ZnCl₂]₂ can also be easily recycled and reused at least up to five runs without any considerable loss in efficiency. To the best of our knowledge, this is the first report of using DES as solvent/catalyst system effectively catalyzing the formation of carbamates from amines, alkyl halides and carbon dioxide. All these facts pointed out the possibility of using this green protocolto facilitate the synthesis of these important compounds for biological studies and designing new drugs.

Experimental

General experimental:

All chemicals were purchased from the Merck, Flucka and Aldrich Chemicals in high purity. The products were characterized by comparison of their spectral and physical data such as NMR, FT-IR, MS, CHNS and melting point with the literature reports. ¹H and ¹³C NMR spectra were recorded with Bruker Avance DPX 250MHz instruments with Me4Si or solvent resonance as the internal standard. Fourier transform infrared (FTIR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Determination of the purity of the substrate and monitoring of the reactions was accomplished by thin-layer chromatography (TLC) on a silica-gel polygram SILG/UV 254 plates.

Preparation of [ChCl][ZnCl]₂ as deep eutectic solvent:^{30, 32}

For the preparation of this deep eutectic solvent, a mixture of choline chloride (10 mmol, 1.39 g) and zinc(II) chloride (20 mmol, 2.72 g) was heated to 100 $^{\circ}$ C until a clear colorless liquid (5 cm³) appeared, then allowed to cool at room temperature and used without further purification.

General procedure for preparation of carbamates (C1-C36):

The 10 mL round bottom flask was charged with amines (1.0 mmol), alkyl halide (1.2 mmol) and $[ChCl][ZnCl_2]_2$ (3 cm^3) and the mixture were stirred for 2h at room temperature under CO₂ atmosphere using balloon set up. After the completion of reaction, the reaction mixture was diluted with water (15 mL) and then, it was neutralized with sodium hydroxide solution (0.1 N). Subsequently, the obtained aqueous solution was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over anhydrous Na2SO4 and concentrated to afford final products. Finally, the obtained crude product was purified by recrystallization from the ethanol. The purity and identity of the product were confirmed by FT-IR, ¹H NMR, ¹³C NMR, and MS. Furthermore, the recovered [ChCl][ZnCl₂]₂ was activated by heating under a reduced vacuum at 70 °C for 30 min and reused for the next cycles.

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The deep eutectic solvents as a green solvent/catalyst system for directly synthesize of carbamates from amines, CO₂ and alkyl halid.