

# Synthesis of carbamates from aliphatic amines and dimethyl carbonate catalyzed by acid functional ionic liquids

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## Abstract

Selective synthesis of carbamates from amines and dimethyl carbonate were studied in the presence of various ionic liquids as catalysts. The  $-SO_3H$ -functionalized ionic liquid was found to be the most active catalyst among the applied ionic liquids, and nearly 100% conversion and 95% selectivity were achieved when using 1,6-hexanediamine as reactant. The acid functional ionic liquid catalyst system is also readily separable and reusable after reaction.

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**Keywords:** Green chemistry; Ionic liquid; Carbamates; Amine; Non-phosgene

## 1. Introduction

Organic carbamates are valuable synthetic intermediates [1] and are widely used for a number of scopes, including drug synthesis [2], production of agrochemicals [3], and polyurethane based polymers and as protecting groups of amines function [4]. These compounds are generally prepared from phosgene [5,6] or phosgene derivatives [7,8] in reaction with corresponding amines, which caused serious environment and safety problems because of the toxicity and corrosion properties of phosgene and hydrogen chloride produced as by-product. Therefore, great efforts have been made for preparation of carbamate compounds using non-toxic reagents and for the development of novel environmentally friendly methodologies. The catalytic carbonylation of nitroaromatics [9] and the oxidative carbonylation of amines [10] are among the most exploited procedures for synthesis of carbamates. However, the toxicity of CO and the deactivation of the noble metal catalyst system made this process very uneconomical. Dimethyl carbonate is a very versatile building block for organic synthesis in green chemistry. The one-step synthesis of carbamates from amines and dimethyl carbonate

therefore is considered to be one of the most attractive routes for its green nature and outlook in practice compared to the conventional methods [11,12]. As a typical research work, Selva et al. [13] reported that good results could be obtained when the reaction was carried out in supercritical  $CO_2$ , but its pressure was very high. Ionic liquids (ILs), as a new kind of solvent and catalyst, were applied in many fields [14–17]. They were also firstly used as solvents and catalysts in the carbonylation of monoamines [18] by our group. However, the concentration of ILs was relatively large and the reaction temperature was relatively high.

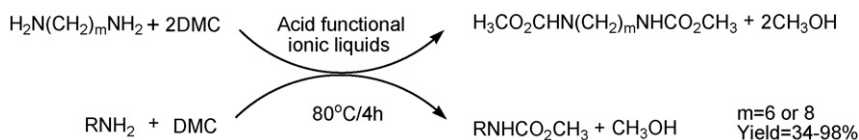
In this manuscript, we reported an efficient and environmentally friendly synthesis of carbamates by carbonylation of amines with DMC using acid functional ionic liquids as catalysts, and high yields were achieved when the amount of ionic liquids were only  $\sim 1$  wt% in comparison with the reactants used (Scheme 1).

## 2. Experimental

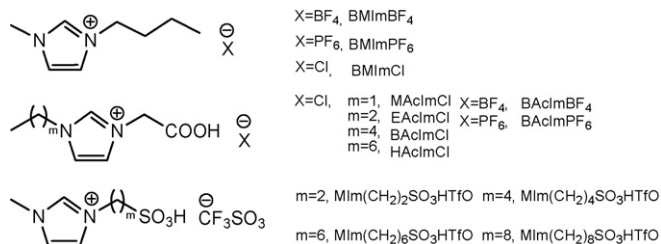
### 2.1. Preparation of ionic liquids

The ionic liquids used in this study, Scheme 2, were synthesized according to the procedures previously reported in literatures [19–23].

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Scheme 1. The reaction of amines and dimethyl carbonate catalyzed by acid functional ionic liquids.



Scheme 2. The ionic liquids used in this study.

## 2.2. General procedure for the reaction of amines with dimethyl carbonate

In order to avoid the reaction between amines and carbon dioxide in air, all reactions were conducted in a stainless autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, the reactants of fixed mol proportion of amine and DMC, and ionic liquids as catalysts were introduced successively without any additional organic solvents. The ratio between monoamine (20 mmol) and DMC (21 mmol) or diamine (20 mmol) and DMC (42 mmol) were 1:1.05 and 1:2.1, respectively. The concentration of ionic liquid in the reaction mixture was 0.6–11 wt% ( $[m_{\text{ionic liquid}}]/[m_{\text{amine}} + m_{\text{DMC}}] \times 100\%$ ). The reaction proceeded at 60–100 °C for 2–8 h. After reaction, the autoclave was cooled to room temperature and 100 ml water was added into the resulted liquid mixtures. The desired resulted product would ‘precipitate’ and solid product could be obtained after filtration, washing, and dryness.

For the reuse investigation of the acid functional ionic liquids as catalysts, 0.82 mol DMC (73.8 g), 0.40 mol 1,6-hexanediamine (HDA, 46.4 g), and 1.2 g (3.26 mmol, 1 wt%)

Table 1  
Results of carbonylation of HDA with DMC in the presence of ionic liquid BMImCl

Entry	Catalyst/mmol (wt%)	T (°C)	t (h)	Conversion <sup>a</sup> (%)	Selectivity <sup>a</sup> (%)
1	0	60	2	1	–
2	4 (11%)	60	2	75	33
3	4 (11%)	60	4	84	37
4	4 (11%)	60	8	84	40
5	4 (11%)	80	4	100	69
6	4 (11%)	100	4	100	65
7	2 (5.5%)	80	4	100	68
8	1 (2.75%)	80	4	100	68
9	0.35 (1%)	80	4	100	67
10	0.2 (0.6%)	80	4	43	18

Reaction conditions: 20 mmol 1,6-hexanediamine, 42 mmol dimethyl carbonate.

<sup>a</sup> The conversion and selectivity were based on the peak area of GC-FID analysis without modification.

ionic liquid MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO were introduced in sequence into the reactor and allowed to react at 80 °C for 4 h. According to the above procedure, after the product was separated from the resulted liquid mixtures, the ionic liquid could also be easily separated from the resulted mixture by filtration and reused for the next time after vacuum distillation at 110 °C and 5 mmHg to remove water.

## 2.3. Qualitative and quantitative analysis

Qualitative and quantitative analysis was conducted with a HP6890/5973 GC/MS and a HP 1790 GC equipped with a FID detector, respectively. The concentration of reactant and product was directly given by the system of GC chemstation according to the area of chromatograph peak.

## 3. Results and discussion

### 3.1. Optimization of reaction conditions

The carbonylation of HDA with DMC was firstly tested at 60 °C in the presence or absence of ionic liquid BMImCl (Table 1). By varying the reaction time from 2 to 8 h, at 60 °C and with 11 wt% catalyst, it was found that 4 h is enough and 37% of hexamethylene dicarbamates (HDC) was produced (entries 1–4). Better results, 69% yield, could be achieved if reacted at 80 °C (entry 5). Determined by GC–MS, *N*-methylation reaction would occur if the reaction was carried out at 100 °C, which would cause the decreasing of selectivity (entry 6). Different concentration of catalyst between 1 and 11 wt% gave similar result but only 18% HDC could form with 0.6 wt% catalyst (entries 7–10). Therefore, 80 °C and 4 h were necessary to obtain a good result. In consideration of the economical and environmental effects, the ideal amount of ionic liquid as catalyst was ~1 wt%.

### 3.2. Carbonylation of HDA with DMC in the presence of different ionic liquids

By applying the optimized reaction condition, 1 wt% catalyst, 80 °C and 4 h, the synthesis of HDC from HDA and DMC were examined with different ionic liquids as catalysts (Table 2). Ionic liquids used in this experiment, compared to catalyst free system, effectively promoted the reaction. In the presence of ionic liquids BMImPF<sub>6</sub> and BMImBF<sub>4</sub> as catalysts, the conversions of 1,6-hexanediamine were 36 and 52% (entries 1–3), although the selectivity to HDC were only 18 and 21%. The –CO<sub>2</sub>H functionalized ionic liquid had higher activity for the reaction and the selectivity to HDC reached to 71% in the presence of HAclmCl

Table 2  
Results of carbonylation of HDA with DMC with different ionic liquids as catalysts

Entry	Ionic liquid	Conversion <sup>a</sup> (%)	Selectivity <sup>a</sup> (%)
1	–	1	–
2	BMImBF <sub>4</sub>	52	21
3	BMImPF <sub>6</sub>	36	18
4	BACImBF <sub>4</sub>	99	27
5	BACImPF <sub>6</sub>	99	32
6	MAcImCl	100	54
7	EAcImCl	100	56
8	BACImCl	100	67
9	HACImCl	100	71
10	MIm(CH <sub>2</sub> ) <sub>2</sub> SO <sub>3</sub> HTfO	100	88
11	MIm(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HTfO	100	93
12	MIm(CH <sub>2</sub> ) <sub>8</sub> SO <sub>3</sub> HTfO	100	95
13 <sup>b</sup>	MIm(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HTfO	100	95
14 <sup>c</sup>	MIm(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HTfO	100	91
15 <sup>d</sup>	MIm(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HTfO	100	92
16 <sup>e</sup>	MIm(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HTfO	100	92

Reaction conditions: 0.4 mol 1,6-hexanediamine, 0.82 mol dimethyl carbonate, 1 wt% ionic liquids, 80 °C, 4 h.

<sup>a</sup> The conversion and selectivity were based on the peak area of GC-FID analysis without modification.

<sup>b</sup> The ionic liquids MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO reused for the second time.

<sup>c</sup> The ionic liquids MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO reused for the third time.

<sup>d</sup> The ionic liquids MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO reused for the fourth time.

<sup>e</sup> The ionic liquids MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO reused for the fifth time.

(entries 4–9). Furthermore, the anion also played an important role in the reaction. The ionic liquids with same BACIm<sup>+</sup> cation but different anions had different activity and the HDC selectivity increased in the sequence of Cl<sup>−</sup>, BF<sub>4</sub><sup>−</sup>, and PF<sub>6</sub><sup>−</sup>. It was also noteworthy that the selectivity of corresponding carbamate went up sharply when using –SO<sub>3</sub>H functionalized ionic liquids, MIm(CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>HTfO, MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO, or MIm(CH<sub>2</sub>)<sub>8</sub>SO<sub>3</sub>HTfO as catalysts and 95% selectivity could be achieved with MIm(CH<sub>2</sub>)<sub>8</sub>SO<sub>3</sub>HTfO (entries 10–12). Whether

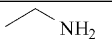

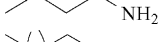
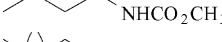
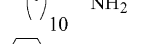

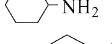



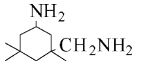
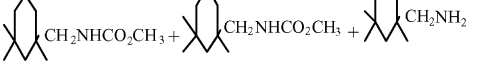
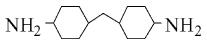
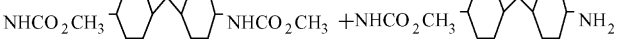


with Cl<sup>−</sup> or TfO<sup>−</sup> as anion, the selectivity of HDC increased with the chain length of N-substituted alkyl of imidazole cations.

The recycling of the acid functional ionic liquid MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO as catalyst was also examined (Table 2). Based on the basic properties of our catalyst and product, carbamate is insoluble but the ionic liquid catalyst is highly soluble in water, the resulted product could be easily separated with the catalyst and the catalyst could be easily reused. It could be seen that there is no obvious loss of catalytic activity in the reaction of 1,6-hexanediamine and dimethyl carbonate after been reused for five times. The conversion of HDA maintained 100% when the catalyst was reused for the fifth time and the HDC selectivity was higher than 90% (entries 13–16). So, the acid functional ionic liquid MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO as catalyst in this reaction was possible to be reused.

### 3.3. The carbonylation of different amines with DMC

Encouraged by the good result obtained with ionic liquid MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO, the reactions of other different amines and dimethyl carbonate were also tested (Table 3). Three typical monoamines, ethylamine, *n*-butylamine and *n*-lurylamine, were firstly investigated. The isolated yields were between 93 and 98% (entries 1–3). For a typical alicyclic amine, cyclohexyl amine, only moderate result was obtained. The yield to methyl cyclohexylcarbamate was 73% (entry 4). For diamine has similar structure as HDA, 1,8-octane diamine (ODA), similar result as HDA to HDC was obtained. The selectivity to the corresponding dicarbamate is 94% (entry 5). Unfortunately, this catalyst system is not effective for the carbonylation of isophorondiamine, which product could be important intermediate for producing of isophorone diisocyanate. The yield to the dicarbamate is only 31% (entry 6). For the preparation of 4,4'-dicarbamatedicyclohexylmethane from 4,4'-diaminodicyclohexylmethane, the yield was only

Table 3  
Results of carbonylation of different amines with DMC in the presence of ionic liquid MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO

Entry	Substrates	Product	Yield <sup>a</sup> (%)
1			93
2			93
3			98
4			73
5			94 (2 <sup>b</sup> )
6			31 (8 <sup>b</sup> )
7			34 (15 <sup>b</sup> )
8			0

Reaction conditions: 20 mmol amine, 21 or 42 mmol dimethyl carbonate, 1 wt% MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO ionic liquids, 80 °C, 4 h.

<sup>a</sup> Isolated yield.

<sup>b</sup> Mono-carbamate.

34% (entry 7). Furthermore, this acid functional ionic liquid MIm(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HTfO was completely inactive for the carbonylation of aromatic amines. Without any methyl phenylcarbamate was obtained with aniline as the starting material. So, this kind of acid –SO<sub>3</sub>H-functionalized ionic liquids is a potentially efficient catalyst system in carbonylation of linear aliphatic amines with DMC, whether monoamine or diamine.

#### 4. Conclusion

In conclusion, a new approach for the synthesis of carbamates from linear aliphatic amines and dimethyl carbonate was developed using acid functional ionic liquids as catalysts. This catalytic system is stable, easily separable, and reusable. Furthermore, this series of acid functional ionic liquids had higher catalytic activity under mild reaction condition without addition of any organic solvents or catalysts.

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