

An efficient ternary catalyst ZnBr₂/K₂CO₃/[Bmim]Br for chemical fixation of CO₂ into cyclic carbonates at ambient conditions



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ABSTRACT

A simple, readily available and recyclable ternary catalytic system of ZnBr₂/K₂CO₃/[Bmim]Br was developed for the efficient conversion of CO₂ and epoxides (both internal and terminal epoxides) to cyclic carbonates under very mild conditions (room temperature, 1 atm) with excellent yields (>90% for 18 examples). The catalytic activity would not be affected by CO₂ in the presence of small amount of water and air. The reactions would even be carried out under CO₂ partial pressure as low as 0.5 atm, giving carbonate in good yield. This process has been repeated 5 times without any obvious decrease in catalytic activity. The influences of the type of catalyst, catalyst loading, CO₂ pressure, reaction time, and temperature on the reaction yields have been investigated. The possible reaction mechanism was proposed based on the reaction results.

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1. Introduction

The conversion and transformation of carbon dioxide (CO₂) into valuable chemicals and materials has been one of the most important and challenging subjects of organic synthesis for the past several decades, due to its economic and environmental benefits [1–6]. One of the most developed reactions for utilization of CO₂ is the synthesis of cyclic carbonates through the ring-expansion addition of CO₂ to epoxides, with 100% atom efficiency [7]. Cyclic carbonates have a wide range of commercial applications, including serving as solvents, fuel additives, electrolytes and chemical intermediate [8–10]. The methodology was developed many years, and the syntheses of ethylene, propylene and butylene carbonates are manufactured commercially worldwide [11]. However, the widely used catalysts for the industrial production still require high pressure of CO₂, high reaction temperature and pure carbon dioxide as feedstock to date [12,13].

From the standpoint of utilization of carbon resources and prevention of global warming, there is a great desire for the development of efficient CO₂ utilizing processes which are operative at lower reaction temperature and pressure, even at ambient conditions. In the past few decades, numerous homogeneous and heterogeneous catalyst systems have been developed,

such as metal oxides [14,15], alkali metal halides [16–18], quaternary ammonium or phosphonium salts [19–24], imidazolium salts or ionic liquids [25–31], and metal complexes [32–37]. However, there are still obvious drawbacks in these systems, such as low catalytic activity, use of pure CO₂ and harsh reaction conditions (high temperature or high pressure). Up to now, the catalyst system which is highly active for the conversion of epoxides into cyclic carbonates at room temperature and ambient pressure of carbon dioxide is relatively scarce [38–40]. Furthermore, most of catalytic systems are only effective for terminal epoxide conversion, therefore, the development of a catalytic system which is effective for internal epoxides under mild conditions is still a big challenge.

N-Heterocyclic carbenes (NHCs) as strong σ -donors have been widely applied in organic catalysis, and their σ -donor character have also been used to capture CO₂ leading to an NHC–CO₂ adduct (imidazolium-2-carboxylates), which were found to be effective organic catalysts for the fixation of CO₂ [41–44]. Previously, we have demonstrated that the NHC–CO₂ adduct generated in-situ is a highly active catalyst for the activation of CO₂ to synthesize cyclic carbonates and quinazoline-2,4-diones as well [45,46]. It is known that *N,N'*-disubstituted imidazolium salts are important precursors in the preparation of *N*-heterocyclic carbenes (NHCs), meanwhile,

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they also have been widely used as ionic liquids (ILs) and 'green' solvents in organic synthesis. Thus, we anticipated that imidazolium-based ILs could serve as precatalyst and solvent for cyclic carbonate synthesis from CO₂. Herein, we report a new ternary catalyst system (ZnBr₂/K₂CO₃/[Bmim]Br) using inexpensive and readily available compounds for the efficient synthesis of cyclic carbonates. This simple, inexpensive and recyclable catalyst system shows significant catalytic activity for the conversion CO₂ with both mono- and di-substituted epoxides to cyclic carbonates under very mild conditions (1 atm or less and room temperature) in excellent yields.

2. Results and discussion

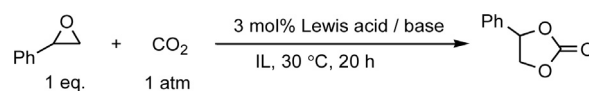
2.1. Effect of reaction conditions

To test the feasibility of our proposed approach, a series of commonly encountered imidazolium-based ILs were selected and explored in the reaction 2-phenyloxirane with CO₂ (Scheme 1). Based on our previous results [45], the reaction was initially carried out with imidazolium salts, K₂CO₃ (3 mol%) as base and the Lewis acid ZnBr₂ (3 mol%) as additive at 30 °C for 20 h under 0.1 Mpa of CO₂ (Table 1). The results showed that all of the tested imidazolium salts were effective precatalyst for this reaction under experimental conditions (Table 1, entries 1–5). However, the catalytic activity of these imidazolium salts depends on the nature of the imidazolium cations and counter ions. Compared to chloride and acetate salts, analogous bromides led to the much higher yield of the product (Table 1, entries 1, 4 and 5), whereas, compared to ethyl and hexyl substituted imidazolium bromides, *n*-butyl substituted bromide gave fairly high yield (Table 1, entries 1–3). This demonstrates that the anion counterparts appear to affect the reaction significantly. This can be explained as Br[−] is a better nucleophile than Cl[−] and OAc[−]. When 1-butyl-3-methylimidazolium bromide ([Bmim]Br) was used, 99% of 4-phenyl-1,3-dioxolan-2-one was obtained with 99% selectivity.

It has been reported that imidazolium-based ILs could convert CO₂ into cyclic carbonate under high pressure (5 bar) and high temperature (150 °C) without adding any additive [47]. To clarify if the reaction would be catalyzed by [Bmim]Br alone, a control experiment catalyzed by [Bmim]Br was performed (Table 1, entry 7). The result revealed that the product was obtained in a low yield (35%). More experiments revealed that the reaction does not occur without [Bmim]Br (Table 1, entry 8). In addition, the yields were decreased dramatically without K₂CO₃ or ZnBr₂ (Table 1, entries 6 and 9), indicating that the existence of base and Lewis acid remarkably enhance the catalytic activity. The effect of different Lewis acids and bases on the CO₂ addition reaction was investigated under the identical conditions. Firstly, Lewis acids ZnX₂ (X = Cl, Br, I), AlCl₃, FeCl₃ and MgCl₂ were investigated. The results showed that all ZnX₂ (X = Cl, Br, I) would promote the reaction (Table 1, entries 1, 10 and 11). However, the reaction rate decreased significantly with AlCl₃ (29%), FeCl₃ (36%) and MgCl₂ (19%) as cocatalyst (Table 1, entries 12–14). Secondly, the effect of the halide ions of ZnX₂ on the reactivity was investigated using

Table 1

Screening of various ILs, bases and Lewis acids for the cycloaddition reaction of CO₂ to 2-phenyloxirane.



Entry ^a	Ionic liquid	Base	Lewis acid	Yield [selectivity] (%) ^b
1	[Bmim]Br	K ₂ CO ₃	ZnBr ₂	99 [99]
2	[Emim]Br	K ₂ CO ₃	ZnBr ₂	75 [99]
3	[Hmim]Br	K ₂ CO ₃	ZnBr ₂	78 [99]
4	[Bmim]OAc	K ₂ CO ₃	ZnBr ₂	40 [99]
5	[Bmim]Cl	K ₂ CO ₃	ZnBr ₂	39 [99]
6	[Bmim]Br	K ₂ CO ₃	–	21 [99]
7	[Bmim]Br	–	–	35 [98]
8	–	K ₂ CO ₃	ZnBr ₂	0 [0]
9	[Bmim]Br	–	ZnBr ₂	32 [98]
10	[Bmim]Br	K ₂ CO ₃	ZnCl ₂	92 [99]
11	[Bmim]Br	K ₂ CO ₃	ZnI ₂	99 [99]
12	[Bmim]Br	K ₂ CO ₃	AlCl ₃	29 [92]
13	[Bmim]Br	K ₂ CO ₃	FeCl ₃	36 [94]
14	[Bmim]Br	K ₂ CO ₃	MgCl ₂	19 [89]
15	[Bmim]Br	Na ₂ CO ₃	ZnBr ₂	82 [99]
16	[Bmim]Br	NaHCO ₃	ZnBr ₂	76 [98]
17	[Bmim]Br	KOAc	ZnBr ₂	83 [99]
18	[Bmim]Br	NaOAc	ZnBr ₂	80 [99]
19	[Bmim]Br	Et ₃ N	ZnBr ₂	95 [99]
20 ^c	[Bmim]Br	K ₂ CO ₃	ZnBr ₂	98 [99]
21 ^c	[Bmim]Br	K ₂ CO ₃	ZnCl ₂	90 [99]
22 ^c	[Bmim]Br	K ₂ CO ₃	ZnI ₂	99 [99]

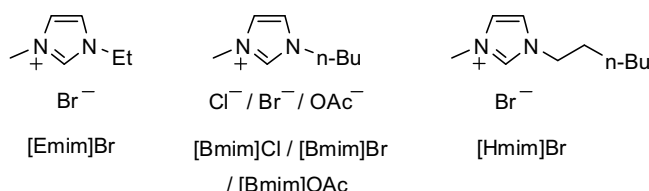
^a Reaction conditions: the reaction was carried out in a 25 mL of Schlenk flask, containing of CO₂ (1 atm), 2-phenyloxirane (1 mmol, 0.11 mL), ionic liquid (2 mmol) and Lewis acid/base (0.03 mmol).

^b GC yield, using dodecane as internal standard and the average of two runs.

^c Reaction conditions: CO₂ (1 atm), 2-phenyloxirane (1 mmol, 0.11 mL), ionic liquid (0.05 mmol), Lewis acid/K₂CO₃ (0.03 mmol).

5 mol% of [Bmim]Br to avoid the effect from large excess of Br[−] introduced by [Bmim]Br, and the results showed that halide ions have a little effect on the catalyst activity with the trend of I[−] > Br[−] >> Cl[−] (Table 1, entries 20–22), which can be explain by the different nucleophilicity of halides. Lastly, the effect of different bases (K₂CO₃, Na₂CO₃, NaHCO₃, KOAc, NaOAc, Et₃N) on the reaction was investigated. Good yields of the product were obtained for all tested bases, including organic base Et₃N.

Next, the influences of reaction time, temperature as well as the loading of ZnBr₂/K₂CO₃ and [Bmim]Br on the reaction were investigated. As shown in entries 1–5 of Table 2, the yield increased with extension of the reaction time from 0.5 to 2 h, whereas, the reaction went to completion after 2 h at 30 °C, indicating that the reaction runs very fast under such mild conditions. Therefore, the effect of temperature on the reaction was investigated in the temperature range of 20–40 °C for 2 h (Table 2, entries 4 and 6–9). The results showed that the reaction went to completion in a wide range of the reaction temperatures (25–40 °C) in 2 h. The effect of ZnBr₂/K₂CO₃ loading on the reaction was investigated in the range



Scheme 1. Structure of selected imidazolium salts.

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