Lewis basic ionic liquids-catalyzed synthesis of 5-aryl-2-oxazolidinones from aziridines and CO_2 under solvent-free conditions†

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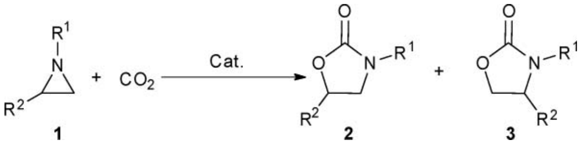
A series of easily prepared Lewis basic ionic liquids were developed as recyclable and efficient catalysts for selective synthesis of 5-aryl-2-oxazolidinones from aziridines and CO_2 without utilization of any organic solvent or additive. Notably, high conversion, chemo- and regio-selectivity were attained when 1-butyl-4-aza-1-azaniabicyclo[2.2.2]octane bromide ([C_4DABCO]Br) was used as the catalyst. Furthermore, the catalyst could be recycled over four times without appreciable loss of catalytic activity. The effects of the catalyst structure and various reaction parameters on the catalytic performance were investigated in detail. This protocol was found to be applicable to a variety of aziridines producing the corresponding 5-aryl-2-oxazolidinones in good yields and excellent regioselectivities. Therefore, this solvent-free process thus represents an environmentally friendly process for ionic liquid-catalyzed conversion of CO_2 into value-added chemicals. A possible catalytic cycle for CO_2 activation induced by nucleophilic tertiary nitrogen of the ionic liquid was proposed, based on studies using *in situ* FT-IR spectroscopy under CO_2 pressure.

Introduction

CO_2 is an easily available renewable carbon resource, which has the advantages of being nontoxic, abundant, and economical.[1–4] One of the few commercial routes using CO_2 as a raw material is the [2+3] coupling between CO_2 and aziridines to afford the 5-membered oxazolidinones[5] (Scheme 1), which are important heterocyclic compounds showing a wide application as intermediates[6] and chiral auxiliaries[7] in organic synthesis. Therefore, the development of green and efficient oxazolidinone production technology has attracted much more attention in chemical industries. From the viewpoint of green chemistry, this cycloaddition procedure utilizing CO_2 as a feedstock is more attractive compared with other processes including carbonylation of amino alcohols with phosgene, CO,[8] and reaction of propargylamines or propargylic alcohols with CO_2.[9]



Scheme 1 Synthesis of 2-oxazolidinones from aziridines and CO_2.

In the past decades, numerous catalysts have been proposed for this reaction, such as a dual-component system, *viz*., salenCr(III)/DMAP,[10] or phenol/DMAP,[11] alkali metal halide,[12] tetraalkylammonium halide system,[12b] iodine,[13] quaternary ammonium bromide functionalized polyethylene glycol,[14] zirconyl chloride[15] and naturally occurring amino acids.[16] In addition, the cycloaddition of aziridines to CO_2 also proceeded smoothly under electrochemical reaction conditions in the presence of nickel complex catalyst.[17] Although significant advances have been made, toxic organic solvents or co-catalysts, high catalyst loading, high CO_2 pressure or long reaction time are generally required to achieve high yields, along with toilsome purification of product and a limited substrate scope in most of the above-mentioned cases. Therefore, developing a low cost, easily preparable, thermally stable and efficient single component catalyst for the conversion of CO_2 to oxazolidinone is still desirable.

Because of their distinctive properties such as high thermal stability, negligible vapor pressure, high loading capacity and easy recyclability, environmentally friendly solvents ionic liquids (ILs) have attracted significant attention from the scientific community.[18] Various chemical reactions have smoothly been performed in ILs.[19] In the framework of our continuous effort on the synthesis of oxazolidinones from CO_2,[14,15] in this work we would like to report an efficient process for the synthesis of 5-aryl-2-oxazolidinones by employing 1,4-diazabicyclo[2.2.2]octane (DABCO)-based Lewis basic ILs as efficient and recyclable catalysts (Scheme 2). Interest in those ILs ([C_{n+1}DABCO]A) stems from their facile preparation from commercially available and relatively inexpensive starting materials, and gratifying thermal behaviour and air/water stability.[20] We previously found DABCO-derived ILs can efficiently catalyze the transesterification reaction.[20d] We envisage that the presence of the tertiary nitrogen in their structure has the potential to form carbamate species with CO_2, assumed to be an activated form of CO_2.[21] Indeed, [C_4DABCO]Br displayed high catalytic

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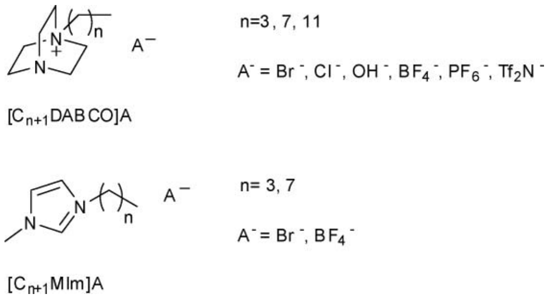


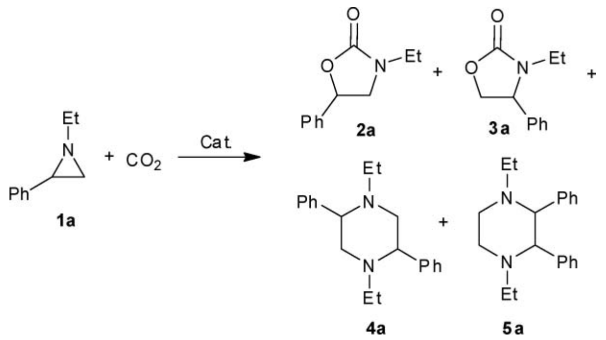
Scheme 2 Ionic liquids used in this study.

activity for this reaction even in the absence of any additional organic solvent or additive. To the best of our knowledge, this is the first example where an IL was used to efficiently catalyze the reaction of aziridines with CO_2. More importantly, the catalyst could be stable during the reaction and can be reused for over four successive cycles without loss of efficiency.

Results and discussion

In the preliminary study, a series of ILs based on $C_{n+1}DABCO^+$ cations and Cl^-, Br^-, OH^-, BF_4^-, PF_6^- or Tf_2N^- anions were used to catalyze the cycloaddition of 1-ethyl-2-phenylaziridine (**1a**) and CO_2. The reaction was carried out at 90 °C and 6 MPa CO_2 for 3 h. For comparison, imidazolium-based ILs were also tested in this study. The results are summarized in Table 1. Obviously, both the cation and anion of the investigated ILs have strong impact on the catalytic activities (entries 1–12, Table 1). Gratifyingly, excellent **2a** yield was achieved with $[C_4DABCO]Br$ as the catalyst (entry 1). The results reveal that both **2a** yield and selectivity decreased markedly as alkyl chain length of the cation increased from C_4 to C_{12} (entries 1, 4, 8), and the same tendency was also found for the imidazolium salt-based IL (entries 9, 11), probably due to alteration of solubility of the ionic liquid in the reaction mixture. Generally, the DABCO-based ILs were more active than the imidazolium ones presumably being ascribed to CO_2's activation by tertiary nitrogen of $C_{n+1}DABCO^+$ (entry 1 *vs.* 9 and 4 *vs.* 11).

Table 1 IL-promoted oxazolidinone synthesis[a]



			Yield (%)[b]		
Entry	Catalyst	Conv. (%)[b]	**2a**	**3a**	**4a + 5a**
1	$[C_4DABCO]Br$	>99	85	4	3
2	$[C_4DABCO]OH$	96	56	2	3
3	$[C_4DABCO]Cl$	77	43	3	3
4	$[C_8DABCO]Br$	>99	75	3	3
5	$[C_8DABCO]BF_4$	85	26	1	4
6	$[C_8DABCO]PF_6$	80	19	1	5
7	$[C_8DABCO]NTf_2$	69	11	1	3
8	$[C_{12}DABCO]Br$	>99	70	3	4
9	$[C_4MIm]Br$	>99	76	3	2
10	$[C_4MIm]BF_4$	85	14	1	2
11	$[C_8MIm]Br$	>99	56	2	2
12	$[C_8MIm]BF_4$	79	20	1	3

[a] Reaction conditions: **1a** (1 mmol, 0.147 g); catalyst loading (1 mol%); CO_2 (6 MPa); 90 °C; 3 h. [b] Determined by GC with biphenyl as an internal standard.

The effect of using ILs with different anions (Br^-, OH^-, Cl^-, BF_4^-, PF_6^-, Tf_2N^-) on the reaction was also investigated. The IL with OH^- showed good activity but lower selectivity (entry 2). On the other hand, halide anions like Cl^-, Br^- gave good results; particularly Br^-, which displayed even more activity than Cl^- (entries 1, 3); whereas, Tf_2N^-, PF_6^- and BF_4^- were found to be inactive (entries 5, 6, 7, 10 and 12). This is understandable, as leaving ability and nucleophilicity would account for their catalytic activity. Therefore, $[C_4DABCO]Br$ was identified as the most effective IL catalyst, and was thus chosen as the model catalyst for further investigation.

Subsequently, the influence of CO_2 pressure on the reaction was investigated under identical reaction conditions (Fig. 1). As is easily seen, pressure has a great influence on the reaction outcome with variation of CO_2 pressure from 1 to 6 MPa. Complete conversion of **1a** and 85% yield of **2a** with 4% of **3a** was obtained at 6 MPa, alongside with small amounts of 1,4-diethyl-2,5-diphenyl-piperazine (**4a**) and 1,4-diethyl-2,3-diphenyl-piperazine (**5a**) being detected by GC-MS and ^1H NMR (see the ESI†). However, conversion and **2a** yield dramatically decreased with further increasing CO_2 pressure. Excessive CO_2 pressure may cause a low concentration of aziridine in the vicinity of the catalyst and retard their interaction, thus resulting in a low efficiency. It is also worth noting that oligomers from homopolymerization of aziridines and copolymerization of aziridines/CO_2 were detected as reported in the literature.[22]

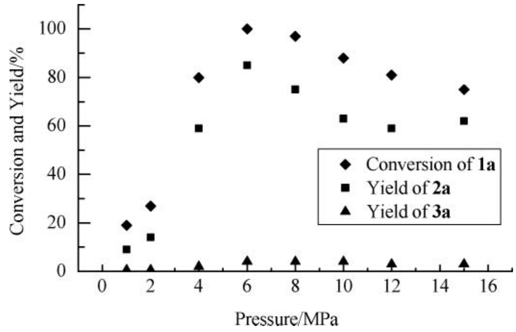


Fig. 1 Conversion and yield *versus* CO_2 pressure. Reaction conditions: **1a** (1 mmol, 0.147 g); catalyst ($[C_4DABCO]Br$, 1 mol%); 90 °C; 3 h.

Fig. 2 shows temperature dependence on the reaction. Obviously, the reaction is sensitive to the reaction temperature. **2a** yield increased sharply with temperature rising from 50 to 90 °C. A further increase in temperature caused a slight decrease in **2a** yield and selectivity, due to facile formation of piperazines **4a** and **5a** at higher temperatures. On the other hand, **3a** could be classified as trace amounts in the temperature range of

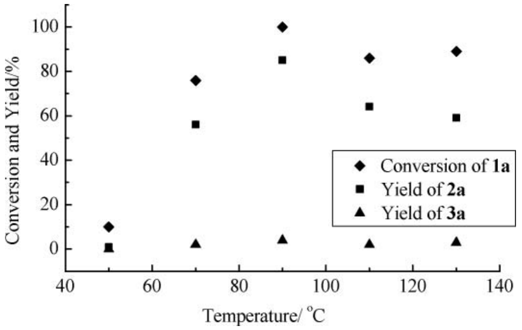


Fig. 2 Reaction temperature dependence of conversion and yield with [C_4DABCO]Br as a catalyst. Reaction conditions: **1a** (1 mmol, 0.147 g); catalyst ([C_4DABCO]Br, 1 mol%); CO_2 (6 MPa); 3 h.

50 to 130 °C. Accordingly, the appropriate reaction temperature would be 90 °C.

Shown in Fig. 3 is the influence of catalyst loading on **2a** synthesis. As easily seen, the catalyst amount has a considerable influence on **2a** yield in the range of 0.1 to 1 mol%. As shown in Fig. 3, **2a** yield was 46% when 0.1 mol% catalyst was used; and thereby increased to 85% as catalyst loading went to 1 mol%. Notably, further increasing the catalyst quantity to 3 mol%, the reaction gave quantitative conversion with 92% of **2a** yield, and 5% of **3a** yield.

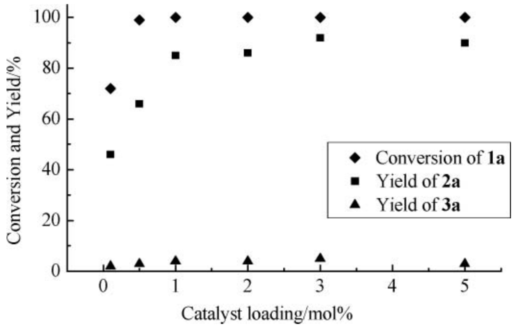


Fig. 3 Influence of catalyst loading on the reaction outcome. Reaction conditions: **1a** (1 mmol, 0.147 g); catalyst ([C_4DABCO]Br); CO_2 (6 MPa); 90 °C; 3 h.

The dependence of **2a** yield and **1a** conversion on reaction time was also evaluated. As shown in Fig. 4, the reaction rate was faster in the initial 3 h and almost full conversion with 85% yield of **2a** was obtained for 3 h. Subsequently, **2a** yield increased slightly to 94% in 8 h, and **3a** yield (3%) was almost invariant during the process.

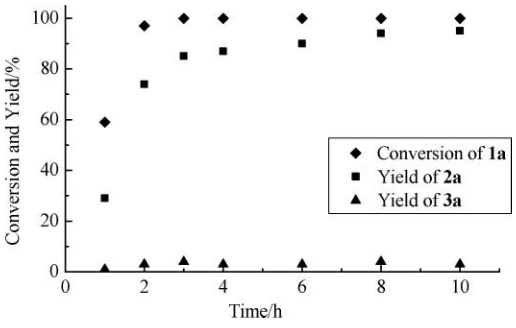


Fig. 4 Dependence of the conversion and yield on reaction time. Reaction conditions: **1a** (1 mmol, 0.147 g); catalyst ([C_4DABCO]Br, 1 mol%); CO_2 (6 MPa); 90 °C.

Table 2 Catalyst reusability[a]

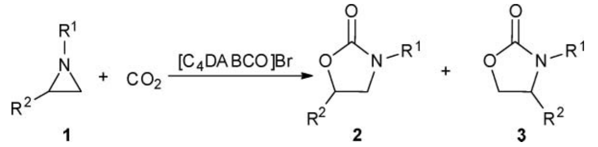
		Yield (%)[b]		
Cycle	Conv. (%)[b]	**2a**	**3a**	**4a + 5a**
1	>99	86	3	3
2	>99	85	4	2
3	>99	87	4	3
4	>99	85	3	4

[a] Reaction conditions: **1a** (5 mmol, 0.735 g); catalyst ([C_4DABCO]Br, 1 mol%); CO_2 (6 MPa); 90 °C; 3 h. [b] Determined by GC.

It is well-known that the stability and reusability of the catalyst system are the two key factors that identify whether it finds potentially practical application in industry. To test catalyst reusability, the reaction was carried out under identical reaction conditions in the presence of a catalytic amount of [C_4DABCO]Br. The catalyst was recovered after the product was separated out by distillation under reduced pressure from the reaction mixture and then used for the next run without further purification under the same conditions.[23] The results as listed in Table 2 indicate that no significant drop in either **2a** yield or selectivity was detected after four successive cycles.

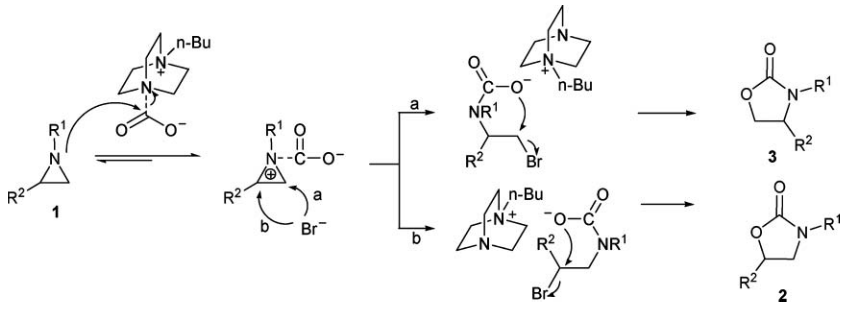
The utility and generality of [C_4DABCO]Br catalyst was also examined. As shown in Table 3, a wide set of oxazolidinones (entries 1–13) were selectively formed in good yields. The 2-phenylaziridine (R^1 = H), although it is easy to form self-oligomers, displayed high chemo-selectivity (entry 1). Especially, aziridines bearing alkyl groups at the nitrogen atom proceeded smoothly (entries 2–11). Increasing steric hindrance of N-substituted group R^1 led to a lower activity (entries 5, 9, 11). In this study, high regioselectivity can also be attained from 96 : 4 (**2**/**3**) to 99 : 1 with variation of alkyl substituent at the nitrogen atom. On the other hand, an electron-donating

Table 3 Various oxazolidinones synthesis[a]



Entry	R^1, R^2	Conv. (%)[b]	Yield of **2** (%)[b]	Regio-selectivity (%)[c]
1	H, Ph	>99	91	96 : 4
2	Me, Ph	>99	86	97 : 3
3	Et, Ph	95	89	97 : 3
4	*n*-Pr, Ph	97	88	97 : 3
5	*i*-Pr, Ph	10	6	97 : 3
6	c-Pr, Ph	95	82	96 : 4
7	*n*-Bu, Ph	99	93	97 : 3
8	*i*-Bu, Ph	79	73	98 : 2
9	*t*-Bu, Ph	15	10	97 : 3
10	Bn, Ph	98	95	97 : 3
11	c-Hex, Ph	19	16	99 : 1
12	Et, *p*-Cl-Ph	85	79	96 : 4
13	Et, *p*-Me-Ph	>99	89	98 : 2

[a] Reaction conditions: **1** (2 mmol); catalyst ([C_4DABCO]Br, 1 mol%); CO_2 (6 MPa); 90 °C; 3 h. [b] Determined by GC. [c] Molar ratio of **2** to **3**.



Scheme 3 The proposed mechanism.

group on benzene ring showed higher activity than an electron-withdrawing group (entry 12 *vs.* 13).

To gain a deeper insight into the reaction mechanism, *in situ* FT-IR spectroscopy under CO_2 pressure was employed to identify the possible intermediates during the reaction. The results are shown in Fig. 5. As previously reported,[21] an amine can react with CO_2 to form the carbamate salt, being considered as an analogue of the adduct formed by the aziridine or $[C_4DABCO]Br$ with CO_2 (Scheme 3).

As shown in Fig. 5(A), the absorption intensity of asymmetric (C═O) vibrations (1780 cm^{-1}) gradually increased over the course of the reaction, indicating *in situ* formation of the carbamic salt $[Et_3N–CO_2]$. Interestingly, absorption peak of the carbonyl group migrated from 1770 cm^{-1} (**1a**-CO_2 or C_4DABCO-CO_2 carbamate salt, Scheme 3) to 1740 cm^{-1} (oxazolidinone) when **1a** was used as the substrate (Fig. 5B, 5C), presumably implying the activation of CO_2 by Lewis basic tertiary nitrogen atom. This would be reasonable that Lewis basic DABCO-derived ILs could significantly promote the reaction. In addition, formation of the carbamate salt from diethylamine and CO_2 was previously confirmed by ^{1}H NMR.[24]

On the basis of previous reports[12a,14] and the experiment results in this work, a possible mechanism for the $[C_4DABCO]Br$-catalyzed cycloaddition of CO_2 with aziridine was proposed as shown in Scheme 3. Firstly, the tertiary nitrogen atom coordinates reversibly with CO_2 to afford the carbamate salt, which could be an activated form of CO_2. Simultaneously, aziridine itself could possibly coordinate with CO_2 to form a positive charge center, which was detected by *in situ* FT-IR under CO_2 pressure. Subsequently, the nucleophilic attack of bromide anion leads to ring opening of the aziridine through two different pathways as represented by paths a and b. The obtained carbamate salt could be stablized by the cation of $[C_4DABCO]Br$. Finally, oxazolidinone is formed by subsequent intra-molecular ring-closure and the catalyst is regenerated. The main product **2** could originate from ring-opening of the aziridine at the most substituted carbon, in agreement with typical ring-opening of three-membered heterocycles.[25]

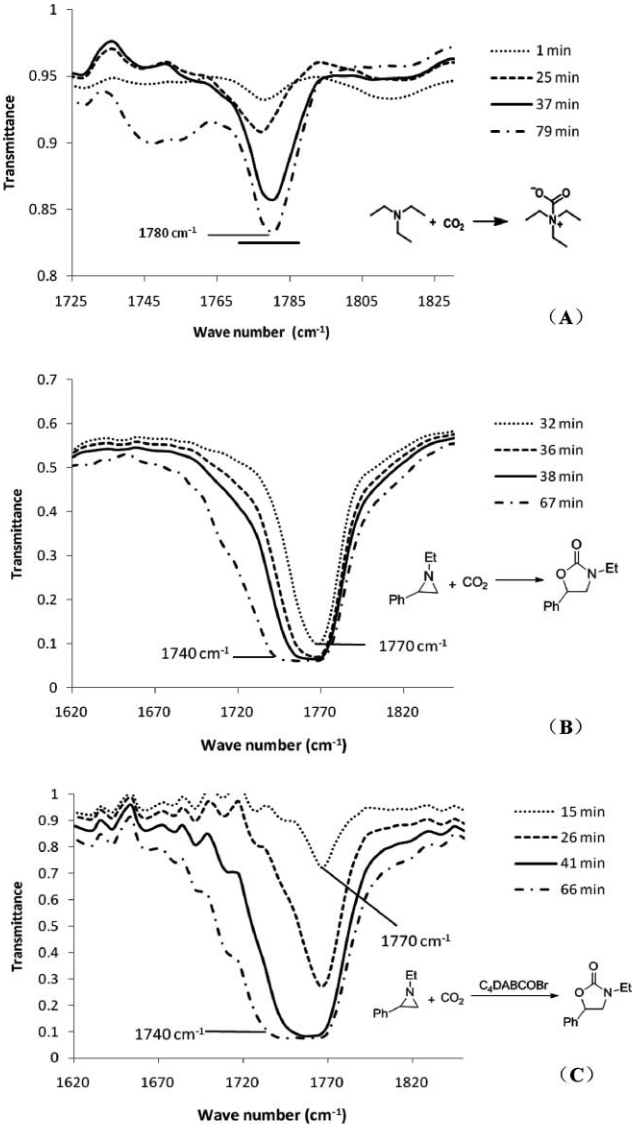


Fig. 5 Results of *in situ* IR spectroscopy under CO_2 pressure monitoring at various reaction time (min). Reaction conditions: (**A**) triethylamine (5 mmol), 120 °C, CO_2 (9 MPa); (**B**) **1a** (5 mmol), 120 °C, CO_2 (9 MPa); (**C**) **1a** (5 mmol), $[C_4DABCO]Br$ (1 mmol), 90 °C, CO_2 (6 MPa). 1780 and 1770 cm^{-1} correspond to peaks for carbonyl group of $[Et_3N–CO_2]$, and $[\mathbf{1a}\text{-}CO_2]/[C_4DABCO\text{-}CO_2]$ carbamic salt, respectively. 1740 cm^{-1} can be absorption of carbonyl group of oxazolidinones.

Conclusions

In summary, for the first time, Lewis basic ILs, such as $[C_4DABCO]Br$, proved to be highly efficient catalysts for the cycloaddition of CO_2 to aziridines under solvent-free conditions. The ILs used in this study represent stable, easily synthesized, cheap, extremely robust and environmentally benign catalysts, which can effectively activate CO_2 through the tertiary nitrogen in the cation part of the IL. The catalyst could be recycled for over four times without loss of yield and selectivity. Therefore, this greener process could show much potential application in industry. Further extending the application of Lewis basic ILs towards other reactions is currently under investigation in our laboratory.

Acknowledgements

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