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Synthesis of bifunctional cyclic carbonates from CO_2 catalysed by choline-based systems

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Abstract

Easily prepared choline iodide is an active catalyst for the synthesis of cyclic carbonates from CO2 and epoxides in ethanol and isopropanol as solvents. With long reaction times good yields of products were obtained at room temperature. Substrates with cyclic carbonate and vinyl or acrylate groups were synthesized with good yields. The heterogenization of the choline over Merrifield resin originates a supported catalyst whit good recyclability.

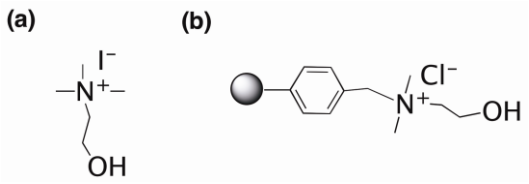
Keywords: Carbon dioxide fixation, Cyclic carbonates, Choline iodide, Green chemistry

Carbon dioxide is an economical, renewable, environmentally friendly but not extensively used carbon source. Its highly functional characteristics, non-toxicity and abundance make this molecule an attractive chemical reagent for organic synthesis.[1] Nevertheless, the use of CO_2 requires an efficient catalytic system, able to overcome the high stability and low reactivity of this molecule.[2]

Chemical fixation of CO_2 by the synthesis of five-membered cyclic carbonates through reaction with epoxides is an interesting synthetic pathway with industrial interests.[3] These products are largely used in organic synthesis as intermediates for the production of fine chemicals, as polar aprotic solvents, electrolyte elements and fuel additives.[4] The great interest in this reaction is evidenced by the diversity of catalysts proposed that include organometallics,[5] *N*-heterocyclic carbenes,[6] alkali metal salts,[7] metal oxides,[8] organic bases,[9] ion-exchange resins,[10] functionalized molecular sieves,[11] phosphonium salts,[12] and polymer-supported ionic liquids (ILs).[13] Simple quaternary ammonium salts (QAS) were the first catalysts used to achieve the cyclic carbonates[14] and present a good compromise between synthesis simplicity and catalytic efficiency.[15]

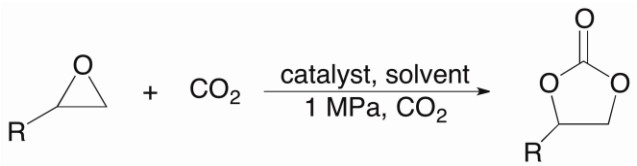
The development of green and sustainable catalysts for this purpose rely on the search for systems that work at room temperature and low pressure of CO_2 with minimum addition of solvents or additives. Aluminium(salen) complexes of North and iron(III) complexes of Kleij and co-workers achieved these requirements.[16] However, to be applied at large-scale, straightforward catalytic solutions must be found without the use of high pressure or temperature, and the need of organic solvents. In this perspective, the study of QAS as catalysts in this reaction is not closed.

Choline is a biological QAS which is easily synthesized by methylation of inexpensive 2-(dimethylamino) ethanol. This QAS has the advantage over others used as catalysts in CO_2 activation of possessing a hydroxyl group that can have a positive effect in the catalytic process.[17] In the form of chloride salt and with $ZnBr_2$ as co-catalyst, choline display high activity for the synthesis of cyclic carbonates from CO_2.[18] On the other hand, choline iodide (ChI) (Scheme 1 **(a)**) with a more reactive counter ion seemed of particular interest to us.



Scheme 1. Schematic representation of choline iodide **(a)** and polymer-supported choline chloride **(b)**.

Herein, we have assessed ChI as a catalyst for the synthesis of cyclic carbonates using green solvents, low pressure of CO_2 (1 MPa) and moderate temperatures (85 ºC) (Scheme 2).



Scheme 2. Synthesis of cyclic carbonates from CO_2 and epoxides.

A set of epoxides was tried for cyclic carbonate synthesis in ethanol as solvent (Table 1). ^{1}H nuclear magnetic resonance (NMR) spectroscopy results (see Supplementary data) show complete conversion of substrates with high selectivity and moderate to high yields. Epoxides **1a**, **2a** and **3a** were also found to be good substrates for the cycloaddition reaction, affording the corresponding cyclic carbonates in excellent yield and selectivity (Table 1, entries 1, 4 and 5). Epichlorohydrin (**4a**) also exhibited good activity but gave the cyclic carbonate with lower selectivity (Table 1, entry 7). Relatively unexplored, but very interesting substrates are the allyl glycidyl ether (**5a**) and glycidyl methacrylate (**6a**) since the products can be used as monomers for double bond polymerization. Both afforded the corresponding cyclic carbonates in moderate to good yield and selectivity (Table 1, entries 8 and 9). It is important to note that the terminal double bond is stable in these reaction conditions. For substrate **7a,** lower conversion was obtained (Table 1, entry 10). Besides terminal epoxides, cyclohexene oxide was also investigated but it gives no product.

The possibility of changing the ethanol for water was investigated for epoxide **1a** under the same conditions. The yield of cyclic propylene carbonate **1b** decreased to 22% but with 99% of selectivity for the cyclic carbonate. The effect of the temperature on the reaction was evaluated. At room temperature, only partial conversion of **1a** was possible (Table 1, entry 2). Addition of potassium iodide (KI) as co-catalyst[19] significantly increased the product yield (Table 1, entry 3).

Table 1
Cycloaddition of CO_2 to terminal epoxides catalysed by ChI in EtOH[a]

Entry	Substrate	Product	Selectivity[b] (%)	Yield[c] (%)
1			99	98
2[d]	**1a**	**1b**	99	77
3[e]			99	99
4	**2a**	**2b**	94	96
5			94	99
6[f]	**3a**	**3b**	94	70
7	**4a**	**4b**	82	68
8	**5a**	**5b**	96	86
9	**6a**	**6b**	86	64
10[g]	**7a**	**7b**	94	46

[a] Reaction conditions: epoxide (14.3 mmol), ChI (0.87 mmol), EtOH (2 mL), CO_2 1 MPa, 85 ºC, 6 h.

[b] Relative molar amounts of the cyclic carbonate determined by NMR spectroscopy of the final mixture.
[c] Isolated yield of products.
[d] Room temperature, 12 h.
[e] Room temperature, 12 h; addition of KI (0.6 mmol).
[f] Conversion: 75%; room temperature, 12 h; addition of KI (0.6 mmol).
[g] Conversion: 63%.

The formation of **1b** was used as a model reaction to study the recyclability of the ChI at 85 ºC and 1 MPa CO_2 for 6 h. After each reaction, the catalyst was filtered off, dried under vacuum and reused for subsequent reactions. As shown in Figure 1, the catalyst could be reused at least 3 times with loss of catalytic activity not significant but in the 4 cycle there is a loss of activity of 20%. Some of this decrease on the activity is related to the loss of catalyst that is used in the next reaction cycle. At final of the third cycle there is a loss of 15% of the catalyst. The yields of the products obtained were similar to those obtained with fresh catalyst, which demonstrates that ChI has good stability and reusability over the reaction runs.

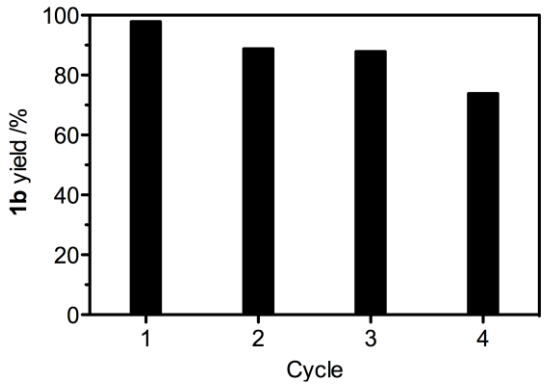


Figure 1. Recycling experiments for ChI. Reaction conditions: **1a** (14.3 mmol), ChI (0.87 mmol), EtOH (2 mL), CO_2 1 MPa, 85 ºC, 6 h.

The lower degree of selectivity observed in certain experiments are probably a result of side reactions. Analysis of the less intense ^{1}H NMR spectra signals enable us to come up with the possibility of the cyclic carbonate aperture by reaction with ethanol, originating the linear carbonate and the respective diol (Scheme 3). As shown in Figures S3-S7 (see Supplementary data), spectra present resonances at 1.23 ppm and 3.44 ppm plausibly assigned to these structures.

Scheme 3. Linear carbonate and diol formation reaction.

Bearing in mind the problem of linear carbonate formation, we investigated the change of solvent to propan-2-ol (IPA) (with lower nucleophilicity) in cyclic carbonate synthesis. From the data presented (Table 2, entries 1-4), it is clear that using this solvent, high yields of products and higher selectivities can be achieved due to the decrease of linear carbonate formation by side reaction effect. When the amount of the catalyst was reduced to a half, the yield of **1b** decreased in almost the same percentage (Table 2, entry 6). With IPA, total conversion of substrate **7a** to the corresponding cyclic carbonate (63% yield) was achieved by addition of an extra amount of catalyst (Table 2, entry 5). Allyl derivative **5a** and acrylate derivative **6a** originate products with increased selectivity in IPA. Using low pressure of CO_2 or room temperature originates low conversions (Table 2, entries 7 and 8). We can also observe that ChI activity is comparable to that of widely used tetrabutylammonium iodide (TBAI) (Table 2, entry 9).

Table 2
Cycloaddition of CO_2 to terminal epoxides catalysed by ChI in IPA[a]

Entry	Substrate	Selectivity[b] (%)	Yield[c] (%)
1	**1a**	99	94
2	**4a**	95	70
3	**5a**	99	84
4	**6a**	96	59
5[d]	**7a**	96	63
6[e]	**1a**	99	53
7[f]	**5a**	98	28
8[g]	**6a**	96	27
9[h]	**1a**	99	99

[a] Reaction conditions: epoxide (14.3 mmol), ChI (0.87 mmol), IPA (2 mL), CO_2 1 MPa, 85 ºC, 6 h.
[b] Relative molar amounts of the cyclic carbonate determined by NMR spectroscopy of the final mixture.
[c] Isolated yield of products.
[d] Addition of more catalyst after 6 h.
[e] ChI (0.44 mmol).
[f] Conversion: 35%; CO_2 0.1 MPa, 85 ºC, 12 h.
[g] Conversion: 30%; room temperature, 24 h.
[h] Catalyst: TBAI.

The heterogenization of the catalyst through the immobilization on a polymeric matrix is the preferable way to assess the possibility of large-scale applications, and several systems have been described for cyclic carbonate synthesis from CO_2.[20] Merrifield resin with functionalized benzylic chlorine was chosen to graft choline and originate polymer-supported choline chloride - PS-ChCl (Scheme 1 **(b)**). The infrared (IR) spectrum of the product, Figure 2 (c), exhibits a broad band at 3100-3700 cm^{-1} region (OH stretching frequencies of ChI) and a medium intensity peak at 1090 cm^{-1} (amine stretching frequency), indicating the successful grafting of choline onto the support. A strong peak centred at 700 cm^{-1} corresponding to the stretching frequency of the $–CH_2Cl$ group in Merrifield resin, Figure 2 (b), has not totally disappeared in the PS-ChCl spectrum, suggesting partial substitution of the available benzylic positions. Elemental analysis for PS-ChCl shows an N content of 3.781% corresponding to 62% of active supported catalyst.

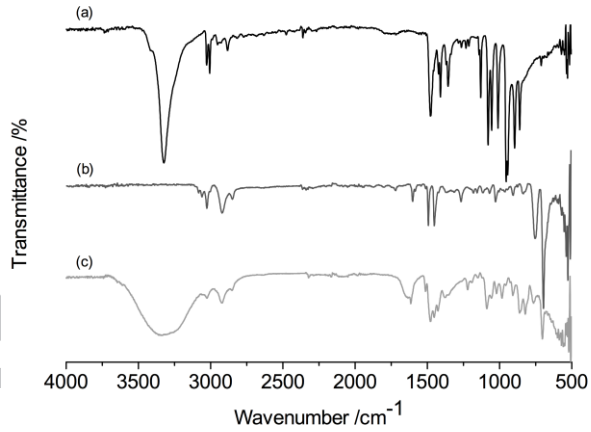


Figure 2. IR spectra of ChI (a), Merrifield resin (b) and PS-ChCl (c).

To survey the applicability of this catalytic system, we examined the cycloaddition reaction of various substrates with CO_2 and the results are summarized in Table 3. We decided to add a small amount of KI to the system due to the beneficial effect of this ion previously observed. A blank experiment with unfunctionalized Merrifield resin and KI was performed under the same conditions and originate **1b** in 29% final yield. The PS-ChCl/KI catalytic system was found to be an efficient system, ensuring high yields of cyclic carbonates and selectivities for epoxides **1a** and **2a** (Table 3, entries 1 and 2) but less active for substrates **5a** and **6a** (Table 3, entries 3 and 4). A comparison with the homogeneous conditions was carried out using an amount of the supported catalyst equivalent to the one previously used in homogeneous conditions and without KI. As expected, the reaction gives less product yield (37%) compared to homogeneous conditions (84%) (Table 3, entry 5).

Table 3
Synthesis of cyclic carbonates catalysed by PS-ChCl/KI[a]

Entry	Substrate	Selectivity[b] (%)	Yield[c] (%)
1	**1a**	99	99
2	**2a**	99	93
3	**5a**	99	76
4[d]	**6a**	96	64
5[e]	**5a**	99	37

[a] Reaction conditions: epoxide (14.3 mmol), PS-ChCl (0.50 g), KI (0.10 g, 0.6 mmol), IPA (2 mL), CO_2 1 MPa, 85 ºC, 12 h.
[b] Relative molar amounts of the cyclic carbonate determined by NMR spectroscopy of the final mixture.
[c] Isolated yield of products.
[d] Conversion: 75%.
[e] Conversion: 65%; PS-ChCl (0.32 g) without KI, 6 h.

A series of catalytic recycling experiments were carried out to survey the regeneration ability of PS-ChCl (Figure 3). The catalyst was simply filtered upon completion of each reaction, washed, dried and reused. Through four successive runs, no significant decrease in **1b** yields was observed suggesting good stability and reusability. On the sixth run, the yield dropped to 66%. The addition of a small amount of KI (0.3 mmol) as co-catalyst, significantly increased the **1b** yield to near the initial values, which points to iodide loss during consecutive cycles. An experiment to study efficiency of catalyst reuse was also performed. With substrate **1a,** a first cycle was carried out under the reaction conditions described in Table 3. Next, an amount of substrate was added without any isolation and another catalytic cycle was run. After four consecutive cycles, 4.4 g of cyclic carbonate **1b** were isolated.

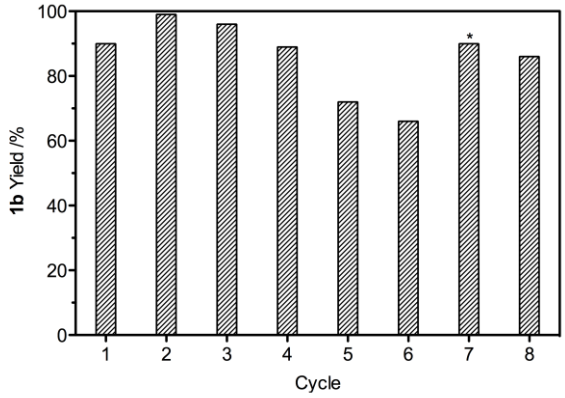


Figure 3. Recycling experiments for PS-ChCl. Reaction conditions: **1a** (14.3 mmol), PS-ChCl (0.50 g), KI (0.10 g, 0.6 mmol), IPA (2 mL), CO_2 1 MPa, 85 ºC, 12 h. *Addition of a new amount of KI.

In summary, we demonstrate a simple and efficient approach using a and recyclable catalyst for the synthesis of cyclic carbonates from CO_2 and terminal epoxides. Particularly relevant is the preparation of bifunctional cyclic carbonates **4b**-**6b** with good yields and excellent selectivities using IPA as solvent. The catalyst derived from choline is easy to prepare and can also be easily immobilized onto a polymeric matrix. The supported catalyst also proved to be efficient in the cyclic carbonate synthesis, undertaking up to eight catalytic cycles.

Experimental

Procedure for the synthesis of choline iodide:
In a Schlenk tube, iodomethane (2.5 mL, 40.2 mmol) was added to a solution of 2-(dimethylamino)ethanol (2.51 mL, 24.9 mmol) in 20 mL of toluene at 0 ºC. The reaction mixture was then allowed to stir at room temperature for 15 h. The crude product was filtered off and the filtrate was washed with diethyl ether, concentrated and dried under vacuum to give ChI as a white solid. ^{1}H NMR (400 MHz, D_2O): δ= 3.06 (s, 9H), 3.38 (t, 2H), 3.91 (m, 2H).

Procedure for the synthesis of polymer-supported quaternary ammonium salt:

A mixture of Merrifield resin (3.0 g), 2-(dimethylamino)ethanol (1.5 mL, 14.9 mmol) and DMF (25 mL) was heated at 65 ºC for 72 h. After cooled down to room temperature, the solid residue was filtered out, washed with water and methanol and dried under vacuum at 30ºC for 24 h. Elemental analysis: O 76.284%, C 64.167%, H 8.336%, N 3.781%.

Cycloaddition procedure for the synthesis of cyclic carbonates:
All the experiments were performed in a 50 mL stainless-steel reactor equipped with a magnetic stirrer and an electric heater. A typical reaction was carried out as follows: **1a** (1.0 mL, 14.3 mmol) was added to a mixture of ethanol (2 mL) and ChI (0.2 g, 0.87 mmol). The temperature was raised to 85 ºC and the reactor was purged with CO_2 (initial pressure: 1 MPa). After the reaction had proceeded for the desired time, the reactor was cooled to room temperature and the remaining CO_2 was removed. The ethanol was evaporated and the reaction mixture was washed with diethyl ether to precipitate ChI. The catalyst was separated and the final product was isolated, dried under vacuum and analysed by NMR spectroscopy.

Acknowledgments

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Supplementary data

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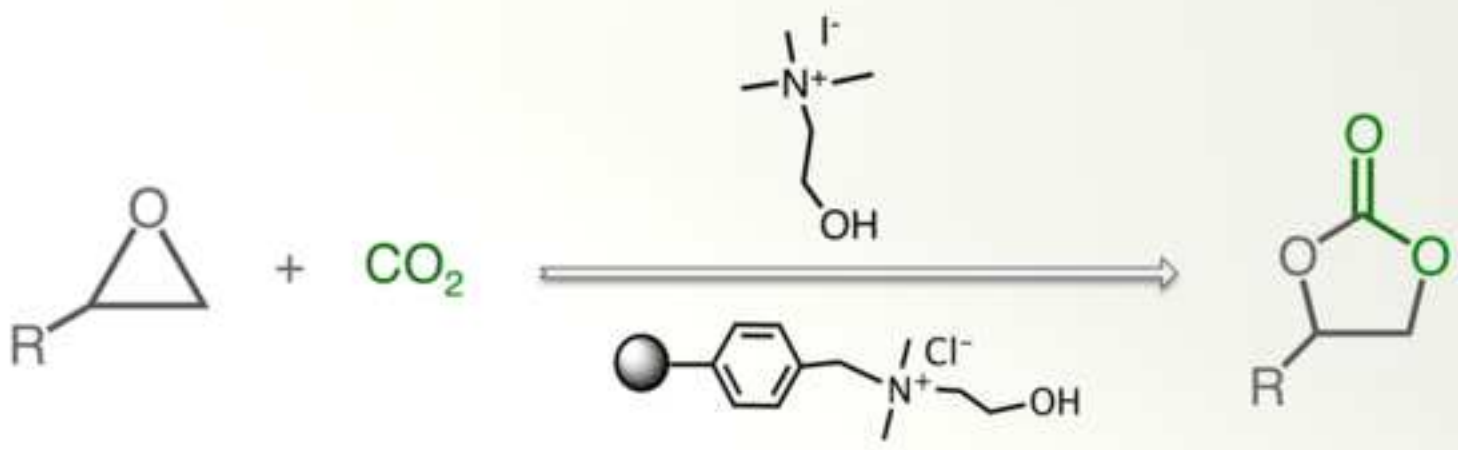

R= $C_5H_7O_2$, C_4H_7O, $C_9H_{15}O_6$