

Choline-based eutectic mixtures as catalysts for effective synthesis of cyclic carbonates from epoxides and CO₂

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ABSTRACT

CO₂ is a renewable, abundant and cheap C1-feedstock and its conversion to cyclic carbonates starting from epoxides has been widely explored in the last years. Nevertheless, conducting this reaction under mild and sustainable conditions is still a challenging task. Herein we present the use of choline-salt based eutectic mixtures as catalysts for the reaction of CO₂ with epoxides to give cyclic carbonates. Choline chloride and choline iodide have been coupled with various hydrogen bond donors (HBDs), mainly cheap and bio-based carboxylic acids and polyols, to form two classes of eutectic mixtures. Very good yields were achieved under mild conditions (80 °C in 7–22 h) for various terminal epoxides, with both classes of catalysts. While a pressure of 0.4 MPa of CO₂ is required to obtain appreciable conversions using choline chloride-based mixture, atmospheric pressure of CO₂ (balloon) has been successfully used with choline iodide-based mixtures. Furthermore, the catalysts could be recycled without appreciable loss of the catalytic activity. The improved catalytic performance of both choline-based eutectic mixtures is attributed to the synergistic activity of the halide, responsible for the opening of the epoxy-ring, and the HBD that has a role in the stabilization of the alkoxide intermediate.

1. Introduction

The possibility to capture and reuse CO₂ is a source of inspiration for numerous research studies [1,2]. CO₂ is a renewable, abundant and cheap C1-feedstock, but its fixation into chemical products is a challenging task because of its high thermodynamic stability [3]. CO₂ conversion to cyclic carbonates starting from epoxides has attracted a lot of attention as an alternative pathway to the use of phosgene [4] and cyanates, and a very large number of catalysts and conditions have been proposed to carry out this reaction [3,5,6]; among them, methods that involve the use of DBU-based organocatalysts, [7,8] organometallic catalysts, [9–13] alkali metal salts, [10] metaloxides [14] and phosphonium salts [15] have been recently reported. The challenge for this kind of reaction is to develop methods that use CO₂ at low pressure and temperature in sustainable solvents or under solventless conditions [16]; several good results have been achieved at room temperature (rt) or with CO₂ atmospheric pressure, especially in the field of organocatalysis [17–20], and also using ionic liquid-type catalysts [21–27].

Quaternary ammonium salts are among the most studied organocatalysts for the conversion of CO₂ in cyclic carbonates, i.e. tetraethylammonium bromide (TEABr) is industrially used to promote the

synthesis of ethylene or propylene carbonate from CO₂ and epoxides since 1950s [28,29]. Their use in neat reactions, without any co-catalysts, usually requires high catalyst loading [30,31] or high temperature and CO₂ pressure [32–34]. Recently many improvements and insights have been made in this context, above all in terms of reaction conditions, due to the growing attention towards sustainable synthesis [6]; to this purpose, some works describe as beneficial the role of an alcoholic or acid component that can be used as a co-catalyst or included in the aliphatic quaternary ammonium salt [35–42]. In fact, the role of both the hydroxyl group and the hydrogen bonds that can be formed in the stabilization of the intermediate after the epoxy-ring opening, proved to be crucial [43,44]. Choline (2-hydroxy-*N,N,N*-trimethylethan-1-aminium) is a bio-based and non-toxic compound bearing both the ammonium and the alcoholic moieties. Choline chloride, bromide or iodide have been largely used for the coupling of various terminal epoxides with CO₂ [43,45–47]. However, Büttner et al. showed that choline halides are ineffective for the synthesis of cyclic carbonates in solventless conditions (2 h, 90 °C, 1 MPa) and an elongation of the alkyl chains of the ammonium ion is required for reaching good conversions [39]. Amaral et al. obtained good results using Choline Iodide (ChI) when ethanol was used as solvent (6 h, 85 °C, 1 MPa) [45].

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Choline derivatives are able to form strong hydrogen bonds acting as hydrogen bond acceptors (HBAs), in the presence of a great variety of hydrogen bond donors (HBDs) [48]. The mixture of the two components (HDB and HBA) has a lower melting point than the components alone, and constitutes what is commonly called Deep Eutectic Solvent (DES) [49–52]. When the components derive from renewable resources, these solvents are called NaDESs (Natural Deep Eutectic Solvents) and they become particularly attractive in the field of sustainable materials and green media for reactions and extraction processes [53,54].

H-bonds have a crucial role in the stabilization of the reaction intermediate formed in the epoxide-to-carbonate cyclization mechanism, so the presence of HBD could be useful to further improve catalytic efficiency of choline salts. In fact, Wu et al. used a choline chloride-PEG₂₀₀(poly ethylene glycole) DES to catalyze the carbonation reaction using a CO₂ pressure of 0.8 MPa and 150 °C [47], while Zhu et al. used choline chloride/urea supported on molecular sieves as heterogeneous catalyst to promote the carbonation reaction with a molar ratio of CO₂: epoxide = 1.5–1.87 at 110 °C [46].

Following our interest in the study of new applications of ionic liquids and DESs [55,56], the aim of the present paper is to exploit the double ability of biobased, non-toxic, recyclable choline-based HBD-HBA pairs to form eutectic mixtures and catalyze under homogeneous conditions the synthesis of cyclic carbonates from epoxides. The carbonation protocols here developed foresee solventless reactions that work in mild conditions of temperature and CO₂ pressure, thus combining efficiency and sustainability. To our knowledge this is the first time that all these aspects are combined together. A table comparing recent homogeneous/heterogeneous IL-type or ammonium-based catalysts appeared in the literature for the synthesis of styrene carbonate from CO₂ and styrene oxide is reported in the supplementary material (Table S2).

2. Experimental section

2.1. Material

All chemicals and solvents were purchased from Sigma-Aldrich or Alfa Aesar and used without any further purification. Particularly hygroscopic reagents (quaternary ammonium salts, glycerol, ethylene glycol and carboxylic acids) were used after vacuum drying and kept in a dryer (see supplementary material, Table S1). CO₂ with $\geq 99.5\%$ purity was purchased from Siad, Italy.

2.2. Synthesis of Choline Chloride (ChCl)-based DES

Choline Chloride (ChCl) was mixed with various HBDs in the appropriate molar ratios, heated at about 80–90 °C (60 °C when the HBD was a dicarboxylic acid) [57] and magnetically stirred until homogeneous liquids were obtained. DESs were cooled to rt before the use and stored in the fridge.

2.3. Representative procedure for the synthesis of carbonates at 0.4 MPa of CO₂ and at 0.1 MPa of CO₂ (balloon)

The reaction at 0.4 MPa was conducted in a stainless-steel, self-made, 25 mL autoclave equipped with a heating mantle. The preformed eutectic mixtures, or the two components of the same (5 % mol in terms of ChCl respect to the epoxide), were weighed inside a 2 mL vial equipped with a magnetic stirring bar; then the epoxide (1.3 mmol) was added. The air in the reactor was firstly replaced with CO₂, then the vial was placed inside the steel autoclave. The autoclave was heated and filled with CO₂ (0.4 MPa), and the vial placed inside was kept stirring for the whole reaction time. After the completion of the reaction, the autoclave was cooled to rt and slowly depressurized.

The reaction at 0.1 MPa was conducted in a 25 ml Schlenk tube equipped with a CO₂ balloon. The two components of the eutectic

mixture (5 % mol respect to the epoxide) were weighed and put inside the Schlenk with the epoxide (2.6 mmol). The air in the Schlenk tube was firstly replaced with CO₂, then the Schlenk was placed in an oil bath heated at 80 °C. The CO₂ of the balloon was then allowed to flow into the flask. After the completion of the reaction, the Schlenk tube was cooled to rt.

In both cases crudes were weighted to check CO₂ incorporation or any reagent loss, and then analyzed by Gas Chromatography–Mass Spectrometry (GC–MS) after dilution in ethyl acetate. Conversions reported in Tables 1 and 2 were calculated by GC–MS using a calibration curve of the starting material in 20–400 ppm range, whereas the selectivity was calculated as ratio between the chromatographic peak of carbonate and the peaks of all by-products detectable by GC–MS. Yields reported in Table 3 were calculated by ¹H NMR using mesitylene as internal standard (see supplementary material for more details); isolated yields are also reported in Table 3. ¹H and ¹³C NMR spectra of the purified products have been acquired after purification of the crude by flash-column chromatography. All obtained carbonates are known, thus they were recognized by comparison with standards or through NMR and mass spectra, matching to what reported in NIST database. The formation of by-products was checked by GC–MS and NMR.

2.4. Procedure for catalyst recycle

The recycle of the catalyst was tested with the best performing mixture Choline Iodide (ChI): Glycerol (1:1) (5 mol%) in the conversion of benzyl glycidyl ether **1b** (2.6 mmol) into the corresponding cyclic carbonate **2b** at p(CO₂) = 0.1 MPa (balloon), 80 °C, for 7 h. After the reaction was completed, ethyl acetate was added to the crude together with a small amount of water. The organic phase was collected to recover the product while the aqueous phase was collected to recover the catalyst after removal of water by distillation. The recovered catalyst was used for next runs without further purification. The organic phase containing the product was analyzed by GC–MS, after dilution as before.

2.5. Instrumentation

GC–MS analyses of reaction mixtures were performed using an Agilent HP 6850 gas chromatograph connected to an Agilent HP 5975 quadrupole mass spectrometer. Analytes were separated on a HP-5MS fused-silica capillary column (stationary phase 5%-Phenyl)-methylpolysiloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness), with helium as the carrier gas (at constant pressure, 36 cm s⁻¹ linear velocity at 200 °C). Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan s⁻¹ within the 12–600 m/z range. The injection port temperature was 250 °C. The temperature of the column was kept at 50 °C for 5 min, then increased from 50 to 250 °C at 10 °C min⁻¹ and the final temperature of 250 °C was kept for 12 min. Epichlorohydrin **1c** and allyl glycidyl ether **1d** (more volatile than the other substrates) were analyzed through the following thermal program: the temperature of the column was kept at 40 °C for 6 min, then increased from 50 to 250 °C at 10 °C min⁻¹ until the final temperature of 250 °C. ¹H NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. ¹³C NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuteriochloroform: 7.26 ppm). Mesitylene (1,3,5-trimethylbenzene) was used as internal standard (see Supplementary material for more details).

3. Results and discussion

The reaction between CO₂ and epoxides catalyzed by eutectic mixtures has been initially studied with styrene oxide **1a** as model substrate at different temperatures and CO₂ pressures.

Under the tested reaction conditions, ChCl and ChI were both insoluble in styrene oxide, but their solubilization increased by coupling

Table 1
Synthesis of styrene carbonate **2a** catalyzed by ChCl-HBD catalysts.

Entry 1a	Catalyst ChCl:HBD	Conversion % ^e	Selectivity % ^e 2a:3a
1	ChCl	0	-
2 ^a	ChCl: Urea (1:2)	33	>99
3 ^a	ChCl: Ethylene Glycol (1:2)	82	93:7
4 ^b	ChCl and Ethylene Glycol (1:2)	80	89:11
5 ^a	ChCl: Glycerol (1:2)	93	98:2
6 ^b	ChCl and Glycerol (1:2)	72	92:8
7 ^a	ChCl: Oxalic Acid (1:1)	76	93:7
8 ^a	ChCl: Citric Acid (1:1)	95	98:2
9 ^a	ChCl: Maleic Acid (1:1)	97	98:2
10 ^{a,c}	ChCl: Maleic Acid (1:1)	91	99:1
11 ^a	ChCl: Malonic Acid (1:1)	97	99:1
12 ^b	ChCl and Malonic Acid (1:1)	92	99:1
13 ^a	ChCl: Tartaric Acid (1:1)	95	95:5
14 ^b	ChCl and Tartaric Acid (1:1)	83	95:5
15 ^a	ChCl: Malic Acid (1:1)	97	99:1
16 ^{a,c}	ChCl: Malic Acid (1:1)	91	98:2
17 ^{a,d}	ChCl: Malic Acid (1:1)	26	98:2
18 ^{b,d}	ChCl and Malic Acid (1:1)	22	98:2
19 ^a	ChCl: Malic Acid (1:1) 1.5%	95	98:2
20 ^a	ChCl: Malic Acid (1:1) 3%	96	98:2

Reaction conditions: 1.3 mmol **1a** (148.6 μL), p(CO₂) = 0.4 MPa, neat.

^a Catalyst was pre-formed as eutectic mixture and then added to **1a**.

^b Catalyst components were added separately in the reaction mixture.

^c p(CO₂) = 0.2 MPa.

^d p(CO₂) = 0.1 MPa (balloon).

^e Conversion and selectivity calculated by GC-MS (see experimental section).

them with a hydrogen bond donor (HBD). Thus, several choline-based eutectic mixtures were prepared and their ability to catalyze epoxides carbonatation was tested. Urea, glycerol, ethylene glycol, water and several carboxylic acids (oxalic, citric, maleic, malonic, tartaric, malic, fumaric, 3-hydroxybutyric, alpha-hydroxyisobutyric, crotonic, benzoic, octanoic, butanoic, and acetic acid), were all tested as HBD. Most of the chosen HBDs are non-toxic and biobased.

3.1. Choline chloride-based catalysts

The activity of ChCl-based catalysts was tested in stainless steel autoclave at maximum p(CO₂) = 0.4 MPa and T = 80 °C (Table 1), as described in the experimental Section 2.3. Eutectic mixtures were initially screened in sub-stoichiometric amounts (5 mol% in terms of choline component with respect to the starting material). A 5% catalyst loading is quite common when carbonatation reactions are performed under mild conditions [31,58,59], and allowed us to easily carry out the subsequent recyclability tests on this small scale.

As already observed [39], ChCl alone had no catalytic effect being very scarcely soluble in the reaction mixture (styrene oxide and CO₂) within 8 h (entry 1); ChCl:Urea (1:2) eutectic mixture behaved slightly better than ChCl alone (entry 2) but definitely better results have been obtained with catalysts containing acidic or alcoholic groups as HBD. All dicarboxylic acids here tested had an excellent activity in terms of both conversion and selectivity; the only exception was oxalic acid (entry 7). All the other ChCl: acids mixtures gave an almost quantitative conversion of **1a** into **2a** (entries 8–20), with a very good selectivity for the formation of **2a**. When polyols were used as HBD, different behaviors were observed: glycerol had an activity similar to that of carboxylic acids (entry 5), while ethylene glycol (entry 3) was less reactive and less selective.

The activity of the catalysts when ChCl-eutectic mixture was pre-formed, as described in experimental Section 2.2 (entries 3, 5, 11, 13,

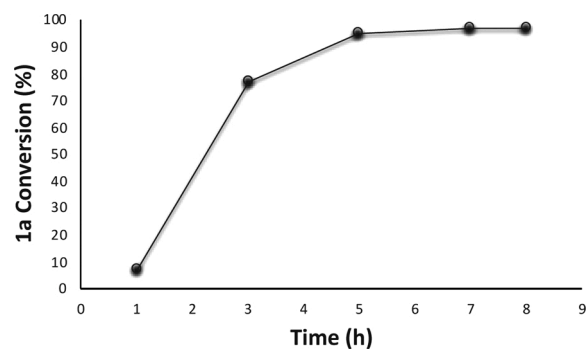
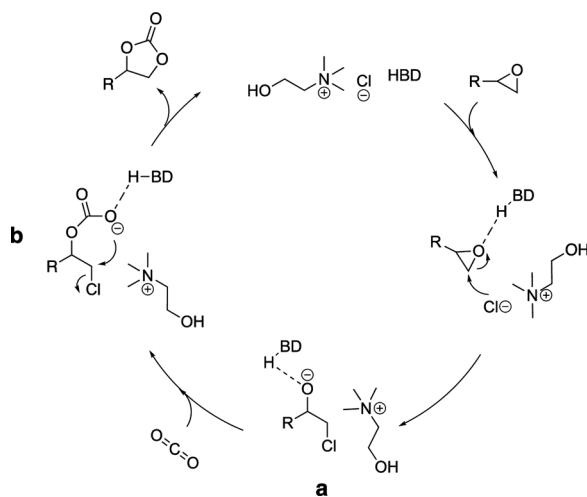


Fig. 1. Effect of the time on **1a** conversion using 5 % ChCl:Malic acid (1:1), 80 °C, p(CO₂) = 0.4 MPa.



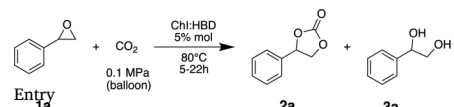
Scheme 1. Proposed mechanism for ChCl-based eutectic catalysts.

the two components are separated by the colon “:”), in comparison to its formation in situ by adding the components separately inside the reaction mixture (entries 4, 6, 12, 14, the two components are separated by “and”), was also analyzed. In some cases, the differences in terms of conversion between the two strategies were negligible (entries 3 and 4, 11 and 12), in other cases they were more relevant (entries 5 and 6, 13 and 14). In terms of selectivity for **2a** formation, the two strategies gave similar results with acids-based mixtures (entries 11 and 12, 13 and 14), but better results were achieved when polyol-based mixture were pre-formed than when they were formed in situ (entries 3 and 4, 5 and 6). The reaction between CO₂ and **1a** was also tested in presence of betaine, a zwitterion, containing both a quaternary ammonium salt, as choline, and an acidic group, but without the halide and hydroxyl groups. As ChCl tested alone (entry 1), also betaine was totally ineffective (data not shown).

Variations of pressure, time and amount of catalyst were further tested by using ChCl: Malic acid (1:1) as catalyst. A decrease in CO₂ pressure proved to be detrimental (entries 10, 16, 17, 18) especially with the system operating at 0.1 MPa (balloon). The addition of the catalyst in the preformed eutectic mixture or as two separate components did not affect conversion if CO₂ pressure was kept at 0.1 MPa (balloon) (entries 17 and 18), whereas a slight decrease in both conversion and selectivity was observed by lowering the catalyst amount (entries 19 and 20). An in-depth study of the initial reaction rate demonstrated that 5–7 h were enough to get an almost quantitative conversion of **1a** (Fig. 1).

On the basis of previous literature studies [6] and the experimental evidences here found, a plausible mechanism was proposed for ChCl-HBD catalyzed reaction of epoxides with CO₂ (Scheme 1). First, epoxide is activated via the hydrogen bond between the HBD and the

Table 2
Synthesis of styrene carbonate **2a** catalyzed by ChI-HBD catalysts.



Entry	Catalysts ChI:HBD	Time (h)	Conversion % ^a	Selectivity % ^a 2a:3a
1	ChI	5	16	99:1
		7	35	
		22	95	
2	ChI and Malic Acid (1:1)	5	88	99:1
		22	95	
3	ChI and Maleic Acid (1:1)	5	87	99:1
		22	95	
4	ChI and Fumaric Acid (1:1)	5	87	98:2
		22	96	
5	ChI and Tartaric Acid (1:1)	5	85	99:1
		22	94	
6	ChI and 3-Hydroxybutyric Acid (1:1)	5	86	99:1
		22	97	
7	ChI and alpha-Hydroxyisobutyric Acid (1:1)	5	77	99:1
		22	97	
8	ChI and Crotonic Acid (1:1)	5	88	>99
		5	87	
9	ChI and Benzoic Acid (1:1)	5	87	>99
		5	87	
10	ChI and Octanoic Acid (1:1)	5	87	>99
		5	76	
11	ChI and Butanoic Acid (1:1)	5	76	>99
		5	90	
12	ChI and Acetic Acid (1:1)	5	90	98:2
		5	91	
13	ChI and Ethylene Glycol (1:1)	5	91	>99
		5	88	
14	ChI and H ₂ O (1:2)	5	88	>99
		5	96	
15	ChI and Glycerol (1:1)	5	96	98:2
		7	99	
16	ChI and Glycerol (1:1) 2%	7	90	97:3
		7	94	
17	ChI and Glycerol (1:1) 4%	7	94	96:4
		7	0	
18	ChI and Glycerol (1:1) 5%, rt	7	0	0
		7	50	
19	ChI and Glycerol (1:1) 5%, 50 °C	7	50	93:7
		7	0	
20	Glycerol 5%	22	0	-
		7	64	
21	TBAI 5%	7	64	>99
		7	64	

Reaction conditions: 2.6 mmol **1a** (297.2 μ L), p(CO₂) = 0.1 MPa (balloon), neat.

^a Conversion and selectivity calculated by GC-MS (see experimental section).

oxygen of the epoxide, facilitating its ring opening that proceeds via nucleophilic attack of the choline halide with the formation of the alkoxide intermediate **a**. Then, intermediate **a** reacts with CO₂ forming **b** that cyclizes to give the cyclic carbonate via chloride elimination. It is noteworthy how the HBD acts as a co-catalyst in the carbonation reaction, helping the stabilization of the intermediates **a** and **b**, through hydrogen bonds and other weak interactions [17,60]. The role of the anion is relevant, since the halide is responsible for both opening the epoxy-ring and as leaving group after ring-closure. For this reason, being iodide a better leaving group than chloride, despite its worse nucleophilicity in such an aprotic environment, ChI-based catalysts were tested.

3.2. Choline iodide-based catalysts

As done for ChCl-HBD mixtures, ChI-HBD mixtures were firstly tested on **1a** (Table 2) as described in the experimental Section 2.3. ChI-based mixtures have higher melting points than ChCl-based ones; for avoiding any possible thermal degradation of the catalyst, that could happen when HBD and HBA were mixed at quite high temperature, the two components (ChI and HBD) were added separately in the reaction mixture (when the two components of the catalysts are added separately their names are divided by “and” instead of the colon, as in Table 1).

From previous studies ChI proved to be ineffective as catalyst at low reaction times (2 h), even with a CO₂ pressure of 1 MPa, in solventless system [39], while Amaral et al. instead demonstrated that it showed a good reactivity in reaction with protic solvents (1 MPa, 6 h) [45]. In our

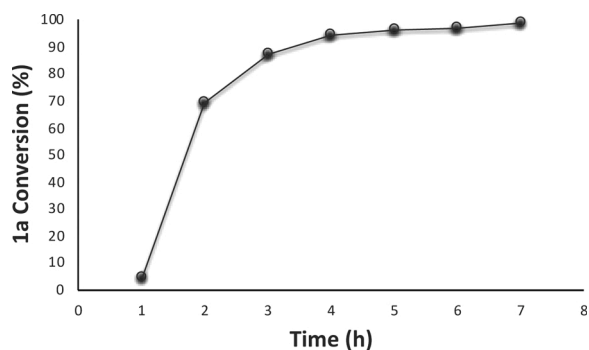


Fig. 2. Effect of time on **1a** conversion using 5 % ChI:Glycerol (1:1), 80 °C, p (CO₂) = 0.1 MPa (balloon).

conditions ChI alone could effectively catalyze the reaction (5% mol, entry 1) giving a 95% conversion of **1a** into **2a** but at longer reaction times (22 h); the most commonly used TBAI (Tetrabutylammonium Iodide) did not give a complete conversion in 7 h (entry 21). The coupling of ChI with a HBD forms a homogenous mixture in a short time, significantly decreasing the carbonation time (entries 2-19, Table 2). Moreover, ChI-based mixtures proved to catalyze the reaction in milder conditions than what found with ChCl-based mixtures, allowing to decrease CO₂ pressure from 0.4 MPa to 0.1 MPa (balloon). Notably, very good results and selectivity were found also by adding the components of the mixture separately inside the reaction system, being iodide a better leaving group than chloride, the product ring-closure is fastened despite the presence of water (Table 2, entry 14) [35,61].

Several HBDs were tested in combination with ChI. When dicarboxylic acids were used as HBDs (entries 2, 3, 4, 5), better conversions (close to 90 %) than those achieved with ChI alone (entry 1) were obtained in shorter reaction times (5 h), demonstrating that the presence of the HBD enhanced ChI activity. High conversions were reached also with other hydroxy-substituted carboxylic acids (entries 6 and 7), crotonic acid (entry 8), benzoic acid (entry 9) and some aliphatic acids (entries 10, 11, 12). Among the various acids, acetic acid seemed to be the most effective. The carboxylic acids tested alone were ineffective (data not shown). When polyols (glycerol and ethylene glycol, entries 13 and 15) or water (entry 14) were used as HBDs, very good results were obtained [35]. The best conversion (99 % in 7 h) was obtained with glycerol as HBD, whereas glycerol used alone (entry 20) was ineffective even after 22 h. By studying in more detail the effect of the catalyst amount, temperature and time it was found that: i) a slight decrease in product conversion was observed by decreasing the catalyst amount (entries 16 and 17); ii) the reaction did not run at rt (entry 18) and just 50 % conversion was achieved at 50 °C after 7 h (entry 19); iii) a conversion of 90% was got after 3 h, becoming quantitative in 7 h (Fig. 2).

3.3. Substrates screening

The catalysts and conditions that gave the overall best results in the carbonation of **1a** (ChCl-Malic Acid under pCO₂ = 0.4 MPa; ChI-Glycerol under pCO₂ = 0.1 MPa) were used for substrate scope (Table 3). Although many other HBDs performed well with ChCl and others with ChI, Malic Acid and Glycerol have been chosen because they are bio-based, non-toxic, widely available and cheap.

Due to the different volatility of the substrates, the reaction with **1c** and **1d** was carried out inside the steel autoclave, in the condition optimized for ChCl-based eutectic mixtures (pCO₂ = 0.4 MPa, 80 °C); this approach guaranteed a greater insulation of the system than the Schlenk tube equipped with CO₂ balloon. In this case it was not possible to carry out reactions inside the autoclave at lower pressures because the small size apparatus would have limited CO₂ amount.

Generally, terminal epoxides could be transformed into the corresponding cyclic carbonates with good to very good yields (entries 1–5);

Table 3
Reaction of various substrates with CO₂ using choline-based catalysts.

Entry	Substrate	Product	By-product	Time (h)	Yield 2 [%] ^c	Yield 3 or 4 [%] ^c
1 ^a				7	90 (88)	9
2 ^a				7	94 (87)	5
3 ^b				7	80 (80)	10
4 ^b				5	91 (80)	8
5 ^a				22	95 (83)	4
6 ^{a,b}			-	23	0	-

^a Reaction conditions: 2.6 mmol of substrate, ChI: Glycerol (1:1) 5%, 80 °C (5^a 100 °C), p(CO₂) = 0.1 MPa (balloon).

^b Reaction conditions: 1.3 mmol of substrate, ChCl: Malic Acid (1:1) 5%, 80 °C, p(CO₂) = 0.4 MPa (autoclave).

^c Calculated by ¹H-NMR (see experimental section), isolated yields in parentheses.

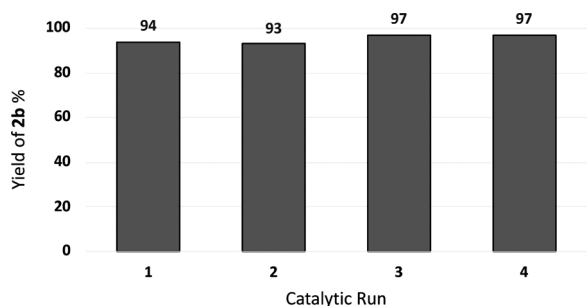


Fig. 3. Catalyst recycling for the conversion of **1b** into **2b**. Yield calculated by GC-MS (see experimental section).

more lipophilic substrate **1e** required a prolonged reaction time. Conversions were quantitative in most cases, just traces (<1 %) of the starting materials were visible at GC-MS. The non-quantitative yields were due to the formation of the corresponding diols of each species as by-product or 1,3-dichloropropan-2-ol for reaction of **1c**.

For internal epoxides (entry 6), no conversion and selectivity were obtained, even when the reaction time was prolonged to 23 h; this discouraged us from studying further non-activated, bio-based or more internal epoxides.

3.4. Catalyst recycles

The recycle of the catalyst ChI: Glycerol (1:1) (5 mol%) was tested in the conversion of **1b** into **2b** in the conditions described above (Table 3, entry 2). After the reaction was completed, ethyl acetate was added to the crude together with a small amount of water. The components of the eutectic mixture are very soluble in water and insoluble in ethyl acetate, in which the synthesized carbonate is soluble instead. The organic phase was collected to recover the product while the aqueous phase was collected to recover the catalyst after removal of water by distillation.

The recovered catalyst was used for next run without further purification. The catalyst could be recycled over four times without appreciable loss of catalytic activity (Fig. 3).

4. Conclusion

Herein sustainable catalysts composed by eutectic mixtures of choline salts and various bio based HBDs have been proved to be effective and recyclable catalysts for the synthesis of terminal cyclic carbonates from CO₂ and epoxides. The HBD, coupled with a choline salt has a dual role: 1) to form an eutectic mixture with the choline salt, soluble in the starting materials in our reaction conditions; 2) to be the co-catalyst in the cycloaddition reaction, being able to stabilize the alkoxide intermediate **a** (Scheme 1). Very good conversions of various terminal epoxides into the corresponding cyclic carbonates were obtained with choline chloride and choline iodide-based catalysts. With both catalysts carbonatation reactions were conducted under solvent-free conditions, at 80 °C, in 7–22 h. While using choline chloride-based mixtures, a pressure of 0.4 MPa of CO₂ was required to obtain appreciable conversions, with iodide-based mixtures atmospheric pressure of CO₂ (balloon) has been successfully used.

The novelty of the present work in the wide panorama of previous studies about choline-based, ionic liquid- or DES- based catalysts is represented by the very mild conditions used (atmospheric CO₂ pressure and temperature below 100 °C) and the simplicity of the catalysts used. In fact, the use of these mixtures presents several advantages: they are very easily synthesized from commercially available, inexpensive and bio-based, non-toxic chemicals and do not require any particular purification step.

CRedit authorship contribution statement

Martina Vagnoni: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Visualization. **Chiara Samori:** Supervision, Writing - review & editing. **Paola Galletti:** Conceptualization, Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2020.101302>.

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