Green Chemistry



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Cite this: DOI: 10.1039/c9gc01165j

Efficient transformation of CO₂ to cyclic carbonates using bifunctional protic ionic liquids under mild conditions[†]

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A series of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) based bifunctional protic ionic liquids (DBPILs) were easily prepared by acid-base reactions at room temperature. They were used to catalyze the cyclo-addition reaction of CO_2 with epoxides under mild conditions. As a metal free catalyst, the best DBPIL showed a 92% yield of products within 6 hours at 30 °C and 1 bar CO_2 without any solvents and co-catalysts. It could afford carbonates in good yields with broad epoxide substrate scope and CO_2 from simulated flue gas (15% $CO_2/85\%$ N₂). IR spectroscopy and DFT studies were carried out to investigate the mechanism of the cycloaddition reaction. The results showed that the DBPILs could activate both CO_2 and epoxides by alkoxy anions and powerful hydrogen-bonding, which was well consistent with experiments.

Received 9th April 2019, Accepted 17th May 2019 DOI: 10.1039/c9gc01165j

rsc.li/greenchem

Introduction

Carbon dioxide is one of the main components of flue gas, which is responsible for global warming. CO₂ is also regarded as an abundant, nontoxic and renewable C1 resource.¹⁻⁴ The utilization of CO2 as a raw material for the production of energy carriers and chemicals is a promising alternative, which can reduce greenhouse gas and thus alleviate the impact of climate change, while producing various organic chemical commodities.⁵⁻¹⁰ However, applications related to CO₂ are limited because of its thermodynamic stability and therefore the CO₂ activation always requires electrolytic reduction processes or a high-energy input.¹¹ One of the typical feasible routes is the synthesis of five-membered cyclic carbonates by cycloaddition of CO_2 with epoxides.^{12–14} As one of the few successful industrial products that efficiently utilize CO2 as a carbon feedstock, cyclic carbonates can be widely used as solvents in chemical processes,^{15–17} electrolyte components in lithium batteries,¹⁸ useful monomers for acyclic carbamates^{19,20} and carbonates,²¹ intermediates in the production of fine chemicals, *etc.*^{22,23}

To date, various catalysts have been developed for the synthesis of useful cyclic carbonates from CO₂ and epoxides, such as metal containing catalysts,²⁴⁻³⁴ organocatalysts,³⁵⁻⁴⁴ ionic liquids etc.⁴⁵⁻⁵⁴ Although most of the catalytic systems show a good yield of carbonates, high temperatures (>100 °C) and/or high CO₂ pressure are always needed in these studies. Hence, great efforts have been focused on the development of efficient and sustainable catalytic systems that can be used for chemically converting CO₂ under relatively mild reaction conditions. In this respect, many catalysts have been synthesized and they exhibited good performance in the synthesis of cyclic carbonates from CO₂. Metal containing catalysts including metalorganic frameworks (MOFs),^{55,56} metal (salen) complexes^{57,58} and metal-porphyrins⁵⁹⁻⁶¹ have been reported to provide a good yield of cyclic carbonates under atmospheric pressure and/or room temperature owing to the active sites of metal ions and halide ions. For example, North and coworkers reported Cr(III) salphen complexes for the cycloaddition reaction under ambient conditions in the presence of TBAB (tetrabutylammonium bromide).²⁹ The catalyst could catalyze CO₂ and epoxides to cyclic carbonates in 57-92% isolated yields after a reaction time of 24 hours. Organocatalytic systems, such as boronic acids,⁶² tetraarylphosphonium salts (TAPS)⁶³ and pyridine-methanol/onium salts,64 could promote the cycloaddition of CO2 with epoxides under moderate conditions due to the activation of epoxides by a hydrogen bond

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[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9gc01165j

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(H-bond). Ionic liquids with a strong hydrogen bond donor (HBD) have been widely reported for this reaction. Gual and Cano et al.⁶⁵ reported an imidazolium based iron-containing ionic liquid, and it showed quantitative conversion and 94% chemoselectivity for the cycloaddition of CO2 to epoxides under near ambient conditions. Park et al.⁶⁶ developed a pyridinium IL-decorated MOF and used it as a solvent-free catalyst for CO₂-oxirane coupling reactions. The best catalyst displayed a high catalytic activity at 60 °C and 1.2 MPa CO₂ because of the synergetic effect of the IL functional sites. In addition, we also demonstrated carboxylic acid-based ionic liquids that could promote the cycloaddition reaction of CO₂ at 50 °C and 0.1 MPa.⁵³ Recently studies have been focused on protic ionic liquids, which exhibited not only an excellent ability of reversible CO₂ capture but also highly efficient CO₂ chemical conversion even under ambient conditions because of the powerful H-bonding.^{67,68} For example, Han et al.¹² employed a novel dual-ionic liquid system for cycloaddition of epoxides with CO₂ at temperatures from 30 to 60 °C at 1 atm, and the results showed excellent yields without any solvents. However, compared to high temperature and pressure catalysts, unsatisfactory activities, a long reaction time (>20 h), and the presence of metals and/or toxic solvents are still drawbacks that need to be overcome. It is a great challenge to design an efficient, green and metal-free catalyst toward effective CO₂ conversion under mild conditions.

Inspired by these studies, we report here the synthesis of DBU-based bifunctional protic ionic liquids (DBPILs) by acidbase reactions at room temperature based on the good acidity of halogenated carboxylic acids and alcohols which is achieved by the inductive effect of the electron-withdrawing group (Fig. 1). DBPILs that were composed of alkoxy anions, protic acid and nucleophilic groups were successfully used in the cycloaddition reaction of CO_2 with epoxides at 1 bar CO_2 and 30/50 °C. We found that they were efficient metal-free catalysts for this reaction, and displayed high activity in producing carbonates without the need for a long reaction time or a co-catalyst. We explored the influence of the substrate scope on the catalytic behaviour with various epoxides and simulated flue gas. DFT studies, IR spectroscopy and experiments were conducted to study the mechanism of the activation of CO_2 and H-bond interactions between DBPILs and epoxides.

Results and discussion

To synthesize the protic ionic liquids, electron withdrawing groups are selected to increase the acidity of alcohols and carboxylic acids through an inductive effect. Halogens are well known as electron-withdrawing groups. It has been proven that Br⁻ is an excellent nucleophilic ion for the cycloaddition reaction in our previous work.48,52 Herein, halogenated carboxylic acids and alcohols with short chain lengths (the closer the halides and acid, the stronger the inductive effect) are chosen to react with superbase DBU. During the experiments, a series of DBPILs composed of protonic acid and nucleophilic groups was prepared by acid-base neutralizing reactions at room temperature. A DBU based ionic liquid with a phenolic hydroxyl group (1d) was prepared using DBU and 4-bromophenol due to the weak acidity of 4-bromophenol attributed to the conjugative effect and the long chain length between the bromide and hydrogen group (details are shown in ESI Scheme S1[†]). 4-Dimethylaminopyridine (DMAP) based ILs (1e) were synthesized according to the literature⁶⁹ (Scheme S2[†]). DBU-based catalysts 1g with NTF₂ were synthesized using an ion-exchange method (Scheme S3[†]). The catalytic activities of various DBPILs were carried out with epichlorohydrin and 1 bar of CO₂ (balloon) in a Schlenk tube at 30 °C. The results are shown in Table 1.

It was found that the common ILs [Bmim]Br (Table 1, entry 1) showed low activity in catalysing the reaction. Interestingly, DBU-based ILs without protonic acid (1a) were observed with a similar activity to [Bmim]Br (Table 1, entry 2 ν s. 1), which indicated that cations may have little effects on the reaction. Then the activity of DBU-based ILs composed of protic acid and bromine ions (1b and 1c) was studied under the same con-



Fig. 1 ILs used in this study.

Table 1 Reactions of CO₂ with epichlorohydrin catalyzed by different ILs^a

	CI	Balloon (99.99%CO ₂)		
Entry	Catalyst	Time (h)	$\mathrm{Yield}^{b}\left(\%\right)$	Selectivity ^b (%)
1 ^c	[Bmim]Br	6	23	>99
2	1a	6	26	>99
3	1b	6	70	99
4	1c	6	76	99
5	1 d	6	14	98
6	1e	6	47	99
7	1f	6	92	99
8	1g	10	4	98
9^d	1f	10	91	99
10^e	$[TMGH^{+}][^{-}O_{2}MMIm^{+}][Br^{-}]^{70}$	12	84	—

^{*a*} Reaction conditions: epichlorohydrin (0.5 ml), ILs (6 mol%), 1 bar of CO₂ (balloon), temperature (30 °C). ^{*b*} Determined by ¹H NMR. ^{*c*} [Bmim]Br = 1-Butyl-3-methylimidazolium bromide (8 mol%). ^{*d*} Catalyst (4 mol%) and temperature (25 °C). ^{*e*} Epichlorohydrin (2 mmol, 0.1850 g), catalyst (0.5 mmol), CO₂ (0.1 MPa), 30 °C, 12 h.

ditions, and they showed a very high yield of chloropropene carbonate (CPC) (70% and 76%, respectively) as compared to 1a without protic acid (Table 1, entries 3 and 4 vs. 2). The probable reason may be that the protic acid of DBPILs could activate epichlorohydrin efficiently by the powerful H-bond interaction. Besides, as a nucleophilic anion, the alkoxy anion might play the same role as Br-, which could increase the active sites. To compare the effect of the H-bond interaction, a DBU based ionic liquid with a phenolic hydroxyl group (1d) was prepared with DBU and 4-bromophbenol. Even the phenolic hydroxyl group has been reported as a good HBD,^{71,72} but in this study, **1d** only showed a low activity of 14%. 4-Dimethylaminopyridine (DMAP) based IL (1e) with a hydroxyl group, which had been reported as an efficient catalyst for this reaction in our previous work,⁵³ was also investigated (Table 1, entry 6). 1e showed a promising yield of CPC (47%) for the hydroxyl group activating epichlorohydrin (Table 1, entry 6 vs. 1, 2), but much lower than DBU based protic ionic liquids (DBPILs). The possible mechanism speculated was that the hydrogen proton from DBPILs had a stronger H-bond interaction with the epoxide than the -OH group from 1e, which made the ring opening of the epoxide much easier, and resulted in the higher activity of DBPILs compared to 1e (Table 1, entries 3, 4 vs. 6). Then, DBPIL 1f incorporated with protonic acid and multi-nucleophilic sites was prepared and used for this reaction. It showed the highest CPC yields of all the catalysts under the same conditions as in the aforementioned studies (Table 1, entry 7). To find whether the alkoxy anion can play the same role with the bromine ion, DBPIL 1g without the bromine ion was prepared and used in this reaction. Only a 4% yield of CPC was obtained after 10 hours as shown in Table 1 (entry 8), which demonstrated that the alkoxy anion had little effect on the catalytic performance of this reaction. However, the selectivity of the DBPILs decreased slightly compared to that of conventional ionic liquids (entries 3, 4, 7, 8 vs. 1, 2), which may be caused by side reactions.^{63,65}

Surprisingly, **1f** showed a 91% yield of CPC within 10 hours at room temperature (Table 1, entry 9), while the reported pincertype compound catalysts,⁷³ which had the highest TON and/or TOF for organocatalysts under ambient conditions, took 24 hours to reach 92% yield of CPC. Furthermore, a comparison of DBPILs with the reported dual-ionic liquid is also displayed in Table 1. The dual-ionic liquid showed an 84% yield of CPC within 12 h, and **1f** exhibited a higher activity, and 92% yield of CPC could be obtained after 6 h (Table 1, entry 10 *vs*. 7). In view of this, **1f** was chosen as a benchmark catalyst to investigate the influence of the reaction parameters.

The effects of the reaction time and temperature are presented in Fig. 2. The yields of CPC increased rapidly to 82% within the first 4 h at 30 °C, and then slowly reached 96% in the next 4 hours. The results indicated an obvious decrease of reaction rates. As the reaction temperature increased to 50 °C, the yield of CPC increased to 98% sharply in 4 h without an



Fig. 2 Effects of the reaction time and temperature when catalyzed by 1f. Reaction conditions: epichlorohydrin (0.5 ml), ILs (6 mol%), CO_2 (balloon).

obvious slow-growth stage. This may be caused by the increasing viscosity of the reaction system with the production of CPC, which has a negative effect on the CO_2 transfer in the liquid phase. The mechanism mentioned above was confirmed by the same behavior from the catalyst loading study shown in Fig. 3, which also showed a slow-growth stage with the increase of **1f**.

 CO_2 is known as the main component of dry flue gas. More attention has been paid to the conversion of CO_2 from the flue gas.^{1,28,34} In order to investigate whether DBPILs could be used in the flue gas, a 15% $CO_2/85\%$ N₂ system was chosen to simulate flue gas for the cycloaddition reaction with epoxides (Scheme 1). However, only 24% of CPC was obtained within 6 hours with catalysis by **1f**, which was much lower than that of pure CO_2 under the same conditions (24% ν s. 92%). The yield of CPC can reach up to 90% after 36 hours of reaction. The results indicated the feasibility for the conversion of CO_2 in the flue gas catalyzed by DBPILs, but the comparably low activity is still a drawback which needs to be overcome.

A range of different substituted terminal epoxides were examined under a balloon of CO_2 condition in the presence of DBPIL **1f**. The results are summarized in Table 2. The terminal epoxide (**2a**) with a bromomethyl group could afford the product **3a** in a good yield of 88% under the optimal conditions. Taking into account the industrial application, the loading of **1f** was reduced, and the reaction temperature increased to 50 °C. However, the carbonate **3b** showed much lower yield than **3c** under the same conditions, which is prob-



Fig. 3 Effects of the catalyst amount when catalyzed by 1f. Reaction conditions: epichlorohydrin (0.5 ml), CO_2 (balloon), temperature (30 °C), reaction time (8 h).



Scheme 1 Cycloaddition of epichlorohydrin with simulated flue gas catalyzed by 1f.

Table 2 Reaction of CO₂ with substrates catalyzed by 1f^a



 a Yields were determined by NMR. b Isolated yields were determined by weighing.



Fig. 4 Recycling experiments with catalysis by 1f. ^a Reaction conditions: 2f (0.5 ml), 1f (6 mol%), 1 bar CO_2 (balloon), temperature (50 °C), reaction time (6 h).

ably due to the high steric hindrance effect. Furthermore, the terminal epoxide (2d) with a phenyl group and glycidol derivatives 2c, 2e-2h were examined. All of these epoxides generated the corresponding cyclic carbonates in good yields (3c-3h).

2f was subsequently chosen as an optimal terminal epoxide to study the cycling performance of DBPIL 1f. When we tried to recycle 1f after the reaction, we found that the isolated yield of 3f decreased obviously from 95% to 77% after four runs (Fig. 4). Based on the report, the reduction of catalytic activity

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after use might be caused by the partial loss of the catalyst for the sublimation property⁶⁷ or catalyst addition to epoxides.^{63,65} Then, a series of experiments were designed to study the reason for the decreased activity (see ESI Scheme S4†). The experiments and spectral results indicated that the DBPIL **1f** could undergo addition to **2f** and further generate **1h** with a hydroxyl group, because of the "super-dissociating" feature of the protic ionic liquids.⁷⁴ Furthermore, **1h** could not activate CO_2 and had a relatively weak H-bond interaction with the epoxide compared to the powerful H-bonding of **1f**, which led to the reduction of the yields in the recycling experiments.

FT-IR spectra were employed to identify whether the alkoxy anion of **1f** could activate CO_2 . As shown in Fig. 5, a new band at 1795 cm⁻¹ appeared after the reaction of CO_2 with **1f**, which corresponded to the new asymmetric (C=O) vibrations of the carbamate salt, thus implying the activation of CO_2 by **1f**.

It has been reported that the H-bond interaction between the catalyst and epoxide can reduce the activation energy of the ring-opening step.48 Hence, a comparison of 1f and 1h catalyzed ring-opening steps was performed by a DFT study to identify whether the hydrogen proton from 1f had a more powerful H-bond interaction with the epoxide than the -OH group from 1h. All calculations were carried out with the B3LYP-D3/6-31+G** level implemented in the Gaussian 09 package. As shown in Fig. 6, the 1h-catalyzed ring-opening step has an energy barrier of 44.2 kcal mol⁻¹, which is slightly higher than that of the **1h**-catalyzed process (39.6 kcal mol^{-1}). The hydrogen atom of **1h** is coordinated with the oxygen of the epoxide through a hydrogen bond leading to an increase of the length of the C-O bond from 1.455 Å to 2.099 Å, which makes the ring-opening much easier. The same interaction can be found between 1f and the epoxide. The hydrogen bond length between 1h and epoxide is 1.601 Å, while that of 1f and epoxide is 1.502 Å, showing a stronger hydrogen bond interaction between 1f and epoxide. The results indicated a higher activity of 1f than 1h due to the stronger H-bond interaction, which was well consistent with our experiment results.



Fig. 5 FT-IR spectra of the activation of CO₂.



Fig. 6 Comparisons of the relative energy of the ring-opening step.

Based on all the results above, a possible mechanism of the **1f**-catalyzed process is proposed, and the DFT study was used to study the mechanism. As shown in Scheme 2 and Fig. 7, the H-bond interaction between **1f** and the epoxide firstly caused an increase of the length of the C–O bond, which could improve the ring-opening process of the epoxide (step 1). The attack of the bromide ion on the epoxide resulted in the ring-opening of the epoxide and made **A** convert into intermediate **B** (step 2) *via* transition state TS1 with a barrier of 39.6 kcal mol⁻¹. When CO₂ was added into the reaction system, it could be activated by the alkoxy anion, and led to the formation of complex **C** (step 3). Subsequently, the alkyl carbonate **D** was generated by the nucleophilic attack of the intermediate



Scheme 2 Mechanism of the cycloaddition reaction catalysed by 1f.



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Fig. 7 Potential energy surface profiles of the 1f-catalyzed process and the optimized geometries for the intermediates and transition states. See the ESI† for computational details.

through TS2 through a low energy barrier of 2.9 kcal mol⁻¹ (step 4). Finally, the cyclic carbonate was obtained by a ringclosure step with an energy barrier of 7.9 kcal mol⁻¹ (TS3). The study illustrated that the epoxy ring-opening step was a rate-limiting step with the highest energy barrier of 39.6 kcal mol⁻¹ (TS1). from experiments, spectroscopy and DFT illustrated the activation of CO_2 of DBPILs and strong H-bond interactions between DBPILs and epoxides. This study provides a high efficiency epoxy ring-opening catalyst for the transformation of CO_2 with the epoxide. The greatly improved catalytic activity makes DBPILs promising environmentally benign catalysts for the applications of CO_2 conversion under mild conditions.

E

Conclusions

In summary, this work exhibits a simple way to prepare DBPILs by introducing electron withdrawing groups to an O–H acid. The DBPILs with protonic acid and nucleophilic sites were used as single-component and metal-free catalysts in the cycloaddition reaction of CO_2 with epoxides under very mild temperature and 1 bar CO_2 conditions. DBPILs showed a great improvement of catalytic activity and good substrate compatibility to various epoxides. Furthermore, DBPILs were found suitable for the conversion of simulated flue gas. The results

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This work is financially supported by the National Key R&D Program of China (2018YFB0605802), the National Natural Science Fund for Distinguished Young Scholars (21425625) and Key Research Program of Frontier Sciences CAS (QYZDY-SSW-JSC011). The support from the Department of Chemical and Biochemical Engineering, Technical University of Denmark are acknowledged. We would further like to thank Dr Dawei Shang and Meng Shi for their kind help.

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