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Efficient Transformation of CO$_2$ to Cyclic Carbonates using Bifunctional Protic Ionic Liquids under Mild Conditions

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ABSTRACT: A series of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) based bifunctional protic ionic liquids (DBPILs) was easily prepared by acid-base reaction at room temperature. They were used to catalyze the cycloaddition reaction of CO$_2$ with epoxides under mild conditions. As a metal free catalyst, the best DBPILs showed a 92 % yield of products within 6 hours at 30 °C and 1bar CO$_2$ without any solvents and co-catalysts. And it could afford carbonates in good yields with broad epoxide substrate scope and CO$_2$ from simulated flue gas (15% CO$_2$/85% N$_2$). IR spectrum and DFT studies were carried out to invest the mechanism of the cycloaddition
reaction. The results showed that the DBPILs could activate both CO₂ and epoxide by the alkoxy anion and powerful hydrogen-bonding, which was well consistence with experiments.

**Introduction**

Carbon dioxide is one of the main components of flue gas, which is responsible for the global warming. CO₂ is also regarded as an abundant, nontoxic and renewable C1 resource.¹⁻⁴ The utilization of CO₂ as raw materials for production of energy carriers and chemicals is a promising alternative, which can reduce greenhouse gas thus alleviate the impact of climate change, whilst 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 high-energy input.¹¹ One of the typical feasible routes is the synthesis of five-membered cyclic carbonates by cycloaddition of CO₂ with epoxides.¹²⁻¹⁴ As one of a few successfully industrial products that efficiently utilize CO₂ as a carbon feedstock, cyclic carbonate can be wildly used as solvents in chemical processes,¹⁵⁻¹⁷ electrolyte components in lithium batteries,¹⁸ useful monomers for acyclic carbamates¹⁹,²⁰ and carbonates,²¹ and 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-based catalysts,²⁴⁻³⁴ organocatalysts,³⁵⁻⁴⁴ and ionic liquids etc.⁴⁵⁻⁵³ Although most of the catalyst systems show a good yield to produce carbonates, high temperatures (>100 °C) and/or high CO₂ pressures are always needed in these studies. Hence, great efforts have been focused on the development of efficient and sustainable catalyst systems that can be carried out chemically converting CO₂ at relatively mild reaction conditions. In this respect, many catalysts have been synthesized and exhibited a good performance in the synthesis
of cyclic carbonates from CO$_2$. Metal-based catalysts including metal-organic framework (MOF),$^{54,55}$ metal (salen) complex$^{56,57}$ and metal-porphyrins$^{58-60}$ were reported to have a good yield of cyclic carbonates at atmospheric pressure and/or room temperature for the activity sites of metal ions and halide ions. For example, North and coworkers reported an Cr(III) salphen complexes for the cycloaddition reaction under ambient conditions with the presence of TBAB (tetrabutylammonium bromide).$^{27}$ The catalyst could catalyze CO$_2$ and epoxides to cyclic carbonates in 57–92% isolated yields after a reaction time of 24 hours. Organocatalyst systems, such as boronic acids,$^{61}$ tetraarylphosphonium salts (TAPS)$^{62}$ and pyridine-methanol/onium salts,$^{63}$ could promote the cycloaddition of CO$_2$ with epoxides under a moderate condition due to the activation of epoxides by hydrogen bond (H-bond). Ionic liquids with a strong hydrogen bond donor (HBD) were widely reported for this reaction. Aitor and Israel et al.$^{64}$ reported an imidazolium based iron-containing ionic liquid, and it showed quantitative conversion and 94% chemoselectivity for the cycloaddition of CO$_2$ to epoxides under near ambient conditions. Park et al.$^{65}$ developed a pyridinium ILs-decorated MOF and used as solvent-free catalyst for CO$_2$-oxirane coupling reactions. The best catalyst displayed a high catalytic activity under 60 °C and 1.2 MPa CO$_2$ 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 CO$_2$ at 50°C and 0.1MPa.$^{52}$ Recently studies have been focused on protic ionic liquids, which exhibited not only excellent ability of reversible CO$_2$ capture but also highly efficient CO$_2$ chemical conversion even under ambient conditions because of the powerful H-bonding.$^{66,67}$ For example, Han et al.$^{12}$ employed a novel dual-ionic liquid system for cycloaddition of epoxides with CO$_2$ under temperature from 30 to 60 °C at 1 atm, the results showed excellent yields without any solvents. However, compared to high temperature and pressure catalysts,
unsatisfactory activities and long reaction time (>20h), presence of metals and/or toxic solvents are still drawbacks that need to be overcome. It is a great challenge that designing an efficient, green and metal-free catalysts toward effective CO\textsubscript{2} conversion under mild conditions.

**Figure 1.** ILs used in this study.

Inspired by these works, we reported here the synthesis of DBU-based bifunctional protic ionic liquids (DBPILs) by acid-base reaction at room temperature based on good acidity of halogenated carboxylic acid and alcohols that caused by inductive effect of the electron-withdrawing group (Figure 1). DBPILs that composed by alkoxy anion, protic acid and nucleophilic groups were successfully used in cycloaddition reaction of CO\textsubscript{2} with epoxides at 1 bar CO\textsubscript{2} and 30/50 °C. We found that they were efficient metal-free catalysts for this reaction, which displayed high activity in producing carbonates without the need for long reaction time or co-catalyst. And we explored the influence of the substrate scope on the catalytic behaviour with various epoxides and simulated flue gas. DFT studies, IR spectrum and experiments were conducted to study mechanism of the activation of CO\textsubscript{2} and H-bond interaction between DBPILs and epoxide.

**Results and discussion**
To synthesize the protic ionic liquids, electron withdrawing groups are selected to increase acidity of alcohols and carboxylic acid through 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.\(^{47,51}\) Herein, halogenated carboxylic acid and alcohols with a short chain length (the closer of the halides and acid, the stronger inductive effect) are chosen to react with super base DBU. During the experiments, a series of DBPILs composed by protonic acid and nucleophilic groups was prepared by acid-base neutralizing reaction at room temperature. DBU based ionic liquid with a phenolic hydroxyl group (1d) was prepared by DBU and 4-bromophenol due to the weak acidity of 4-bromophenol attributed to the conjugative effect and the long chain length between bromide and hydrogen group (Details are shown in supporting information Scheme S1). 4-dimethylaminopyridine (DMAP) based ILs (1e) were synthesized according to the literature.\(^{68}\) (Scheme S2). DBU-based catalysts 1g with NTF\(_2\) was synthesized with ion-exchange method (Scheme S3). The catalytic activities of various DBPILs were carried out with epichlorohydrin and 1 bar of CO\(_2\) (balloon) in a schlenk tube at 30 °C. The results were shown in Table 1.

**Table 1: Reactions of CO\(_2\) with epichlorohydrin catalyzed by different ILs\(^a\)**

| Entry | Catalyst | Time (h) | Yield\(^b\) (%) | 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     | 1d       | 6        | 14              | 98                   |
| 6     | 1e       | 6        | 47              | 99                   |
| 7     | 1f       | 6        | 92              | 99                   |
| 8     | 1g       | 10       | 4               | 98                   |
It was found that the common ILs [Bmim]Br (Table 1, entry 1) had a low activity in catalysing the reaction. Interestingly, DBU-based ILs without protonic acid (1a) was observed a similar activity with [Bmim]Br (Table 1, entry 2 vs 1), which indicated that cation may have little effects on the reaction. Then the activity of DBU-based ILs composed by protic acid and bromine ion (1b and 1c) was studied at the same conditions, and showing a very high yield of chloropropene carbonate (CPC) (70% and 76% respectively) as compared to 1a that without protic acid (Table 1, entry 3, 4 vs 2). The probable reason maybe that the protic acid of DBPILs could activate epichlorohydrin efficiently by the powerful H-bond interaction. Besides, as a nucleophilic anion, alkoxy anion might play the same role with Br⁻, which could increase the active site. To compare the effect of H-bond interaction, DBU based ionic liquid with a phenolic hydroxyl group (1d) was prepared by DBU and 4-bromophenol. Even phenolic hydroxyl group was reported a good HBD⁶⁹,⁷⁰, but in this study, 1d only showed a low activity of 14%. 4-dimethylaminopyridine (DMAP) based ILs (1e) with a hydroxyl group, which had been reported as an efficient catalyst for this reaction in our previous work,⁵² 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 was speculated that hydrogen proton from DBPILs had a stronger H-bond interaction with epoxide than –OH group from 1e, which made the ring open of epoxide much easier, and resulted in the higher activity of DBPILs compared to 1e (Table 1, entries 3, 4 vs 6). Then, DBPILs 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 at the same conditions with
aforementioned studies (Table 1, entry 7). To find whether alkoxy anion can play the same role with bromine ion, DBPILs 1g without bromine ion was prepared and used in this reaction. Only 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 catalytic performance of this reaction. Surprisingly, 1f showed a 91% yield of CPC within 10 hours at room temperature (Table 1, entry 9), while the reported pincer-type compounds catalysts, which had the highest TON and/or TOF for organocatalysts under ambient conditions, took 24 hours to reach 92% yield of CPC. In view of this, 1f was chosen as benchmark catalyst to investigate influence of reaction parameters.

Figure 2. Effects of reaction time and temperature catalyzed by 1f. Reaction conditions: epichlorohydrin (0.5ml), ILs (6 mol%), CO₂ (balloon).
Figure 3. Effects of catalyst amount catalyzed by 1f. Reaction conditions: epichlorohydrin (0.5ml), CO$_2$ (balloon), temperature (30 °C), reaction time (8 h).

The effects of reaction time and temperatures were presented in Figure 2. The yields of CPC increased rapidly to 82% within the first 4 h at 30 °C, then slowly reached to 96% in the next 4 hours. The results indicated an obviously 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 obvious slow-growth stage. This may be caused by the increasing viscosity of the reaction system with the producing of CPC, which have a negative effect on the CO$_2$ transferring in the liquid phase. The mechanism mentioned above was confirmed by the same behavior of the catalyst loading study shown in Figure 3, which also had a slow-growth stage with the increasing of 1f.

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

CO$_2$ is known as the main component of dry flue gas. More attentions has been paid on the conversion of CO$_2$ from the flue gas.$^{1,2,6,32}$ In order to investigate whether DBPILs could be used in the flue gas, a 15% CO$_2$/85% N$_2$ 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 catalyzed by 1f, which was much lower than pure CO$_2$ at the same conditions (24% vs 92%). The yield of CPC can reach to 90% after 36 hours reaction. The results indicated the feasibility for conversion of CO$_2$ in the flue gas catalyzed by DBPILs, but the comparably low activity was still the drawback need to be overcome.

Table 2: Reaction of CO$_2$ with substrates catalyzed by 1f
A range of different substituted terminal epoxides were examined under a balloon of CO$_2$ condition in the presence of 1f DBPILs. The results were summarized in Table 2. Epibromohydrin (2a) could afford the product 3a in a good yield of 88% at the optimal condition. Taking into account of 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 at the same condition, which probably due to the high stereo-hindrance effect. Furthermore, styrene oxide 2d and glycidol derivatived 2e-2h were examined. All of these epoxides generated the corresponding cyclic carbonates in good yields (3d-3h).
Figure 4. Recycle experiments catalyzed by 1f. \(^a\) Reaction conditions: 2f (0.5 ml), 1f (6 mol%), 1bar CO\(_2\) (balloon), Temperature (50 °C), Reaction time (6 h).

2f was subsequently chosen as an optimal terminal epoxide to study the cycling performance of DBPILs 1f. When we tried to recycle 1f after the reaction, we found that the yield of 3f decreased obviously from 95% to 77% after four runs (Figure 4). Based on the report, the reduction of catalytic activity after used might be caused by the partial loss of the catalyst for the sublimation property\(^66\) or catalyst addition to epoxides\(^62,64\). Then, a series of experiments were designed to study the reason of the decreased activity (See Supporting Information Scheme S4). The experiments and spectrum results indicated that the DBPILs 1f could addition to 2f and further generate 1h with a hydroxyl group, because of the “super-dissociating” feature of the protic ionic liquids.\(^72\) Furthermore, 1h could not activate CO\(_2\) and had a relatively weak H-bond interaction with epoxide compare to the powerful H-bonding of 1f, which led to the reduction of the yields in the recycle experiments.
**Figure 5.** FT-IR spectra of the activation of CO₂

FT-IR spectra were employed to identify whether alkoxy anion of 1f could activate CO₂. As shown in Figure 5, a new band at 1795 cm⁻¹ appeared after the reaction of CO₂ with 1f, which corresponded to the new asymmetric (C=O) vibration of the carbamate salt, thus implying the activation of CO₂ by 1f.

**Figure 6.** Comparisons of the relative energy of the ring-opening step.
It is reported that H-bond interaction between catalyst and epoxide can reduce the activation energy of ring-opening step.\textsuperscript{47} Hence, comparison of 1f and 1h catalyzed ring-opening step was examined by DFT study to identify whether hydrogen proton from 1f had a more powerful H-bond interaction with epoxide than –OH group from 1h. All calculations were carried out with B3LYP-D3/6-31+G** level implemented in Gaussian 09 package. As shown in Figure 6, 1h-catalyzed ring-opening step has an energy barrier of 44.2 kcal/mol, which is a little higher than 1h-catalyzed process (39.6 kcal/mol). The hydrogen atom of 1h is coordinated with the oxygen of epoxide through a hydrogen bond leading to the length of the C–O bond increased from 1.455 Å to 2.099 Å, which makes the ring-opening much easier. The same interaction can be found from 1f and epoxide. The length of hydrogen protons of 1f and oxygen of epoxide is closer than 1h (1.502 Å), the increased length of the C–O bond caused by hydrogen bond of 1f and epoxide is a little longer (from 1.455 Å to 2.102 Å) than 1h. 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.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{cycloaddition.png}
\caption{Scheme 2. Mechanism of the cycloaddition reaction catalysed by 1f.}
\end{figure}
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 Figure 7, the H-bond interaction between 1f and epoxide firstly made the length of C-O bond increased, which could improve the ring-open process of epoxide (step 1). The attack of bromide ion to epoxide resulted in the ring-open of epoxide and made A convert into intermediate B (step 2) via
transition state TS1 with a barrier of 39.6 kcal/mol. As CO$_2$ was added into the reaction system, it could be activated by alkoxy anion, and led to the formation of complex C (step 3). Subsequently, the alkyl carbonate D generated by the nucleophilic attack of the intermediate through TS2 through a low energy barrier of 2.9 kcal/mol (step 4). Finally, the cyclic carbonate was obtained by ring-closure step with an energy barrier of 7.9 kcal/mol (TS3). The study illustrated that the epoxy ring-opening step was a rate–limited step with the highest energy barrier of 39.6 kcal/mol (TS1).

**Conclusions**

In summary, this work exhibits a simple way to prepare DBPILs by introducing electron withdrawing groups to 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 at 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 from experiments, spectrum and DFT illustrated the activation of CO$_2$ of DBPILs and strong H-bond interaction between DBPILs and epoxide. This study provides a high efficient epoxy ring-open catalyst for transformation of CO$_2$ with epoxide. The greatly improved catalytic activity makes DBPILs a promising environmentally benign catalyst for the applications of CO$_2$ conversion at mild conditions.

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Conflicts of interest

The authors declare no conflicts of interest.

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