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Hydrogen bonding-inspired organocatalysts for CO_2 fixation with epoxides to cyclic carbonates

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ABSTRACT

Carboxyl-containing organocatalysts, e.g. EDTA (ethylenediaminetetraacetic acid) in combination with nucleophilic halide such as nBu$_4$NBr were demonstrated to be efficient catalyst systems for the synthesis of cyclic carbonates from CO_2 and a broad range of epoxides in excellent yield and selectivity. Thanks to synergistic effects of carboxylic groups and bromide anion, the cycloaddition reaction proceeded smoothly at 5 bar CO_2 under mild reaction conditions. Interaction of carboxylic groups in EDTA with the epoxide via hydrogen bonding presumably facilitates the ring-opening of the epoxide by the nucleophile e.g. bromide. In particular, multiple carboxylic groups in one molecule i.e. EDTA could more effectively activate the epoxide and stabilize the alkoxide intermediate through multi-site hydrogen bonding in comparison with monocarboxylic acid. Moreover, the carboxylic acid like EDTA used in this study represents a cheap, commercially available, environmentally benign, metal-free catalyst for CO_2 conversion. Thus, this catalytic protocol could have potential application for catalytic fixation of CO_2 into value-added chemicals.

1. Introduction

With the increasing environmental and societal concerns about global warming associated with carbon emission, great efforts have been devoted to carbon dioxide fixation during the past two decades. Indeed, CO_2 has been widely used as a potential C_1 building block for the production of various chemical products, as it is nontoxic, economical and abundant [1–4]. However, the biggest drawback associated with CO_2 utilization is its thermodynamic stability and kinetic inertness. Therefore, developing efficacious catalysts with designing elaborate substrates would be crucial to performing CO_2 fixation successfully. One promising methodology in this area is the insertion of CO_2 into epoxides to afford cyclic carbonates as shown in Scheme 1. This reaction is 100% atom-efficient and eco-friendly, being coincident with criteria of green chemistry and sustainable development. In addition, cyclic carbonates are an important class of chemical products, which are widely used as polar aprotic solvents, electrolytes in secondary batteries, valuable monomers in the synthesis of polycarbonates and polyurethanes, and as intermediates in the manufacture of fine chemicals [5–8].

In the past decades, various metal catalytic systems have been developed in particular transition metal catalysts such as metal-Salen [9,10], metal-porphyrin [11,12], and metal organic framework (MOF) system for the cycloaddition reaction [13,14]. On the other hand, with regard to environment acceptable and economical procedures, metal-free catalysis, i.e. organocatalysis has been proved to be an easily available, inexpensive, devisable and powerful alternative [15,16]. Outstandingly, a number of organocatalysts perform well in the coupling of CO_2 and epoxides, in comparison with transition metal catalysts under comparable reaction conditions (below 10 bar and 100 °C) [17–20]. Among the active organocatalysts, hydrogen-bonding donors (HBD) hold important status probably due to efficacious activation of the epoxide via hydrogen bonding [21–26]. Kleij et al. have screened various phenolic organocatalysts using tetrabutylammonium iodide (TBAI) as co-catalyst. In this system, pyrogallol showed good catalytic reactivity under 10 bar CO_2 at 25–45 °C [21]. Soon afterwards, the pentaerythritol/TBAI-catalyzed cycloaddition reaction of CO_2 with epoxides was found to proceed smoothly under 4 bar CO_2 [22]. Furthermore, a series of hydroxyl-functionalized ionic liquids [23–25] were also proved to be highly efficient catalysts for the cycloaddition reaction in the absence of any co-catalysts under similar reaction conditions. Very recently, dinaphthyl silanediol/TBAI

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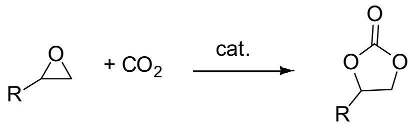
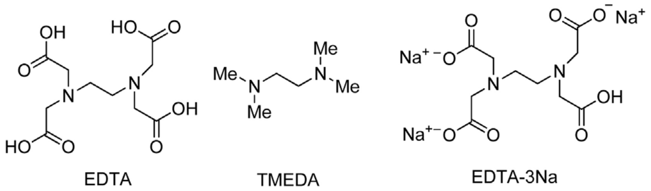


Scheme 1. Cycloaddition of CO_2 with epoxide.



Scheme 2. EDTA, TMEDA and EDTA-3Na used in this study.

catalytic system was developed even at atmospheric pressure of CO_2 and room temperature to prepare cyclic carbonates [26]. However, the complicated procedure is required for the catalyst preparation.

As a kind of HBD, carboxylic acids are alternatives to alcohols and phenolic compounds. This could be understandable because carboxylic group could coordinate with oxygen atom in the epoxide through hydrogen bonding interaction, thus facilitating ring-opening of the epoxide. In this aspect, Han et al. employed betaine-based salts bearing with carboxyl group as catalysts for the synthesis of cyclic carbonates from epoxides and CO_2. As a result, the reaction could proceed smoothly under 8 MPa CO_2 and at 140 °C [27]. Subsequently, milder reaction conditions (2 MPa, 125 °C) was realized for the cycloaddition of epoxides with CO_2 catalyzed by bifunctional carboxylic-functionalized ionic liquids [28]. Inspiringly, CO_2 pressure could reduce to 1 MPa when amino acid ionic liquids were applied as catalysts at 120 °C [29]. Although significant advances have been made, performing the cycloaddition of epoxides and CO_2 under mild reaction conditions especially at low pressure (ideally at 1 bar) could be desirable and still remains a challenge.

Ethylenediaminetetraacetic acid (EDTA, Scheme 2) is commonly used as a complexing agent in analytical and environmental chemistry due to the advantageous characters of being nontoxic, cheap and commercially available [30,31]. EDTA with carboxylic group could be potentially used as an excellent hydrogen-bonding donor. Furthermore, we envisioned that multiple carboxylic groups in one molecule, e.g. four carboxylic groups in one EDTA molecule, could more effectively activate the epoxide through multi-site hydrogen bonding compared with single-site hydrogen bonding, and thereby greatly promote the cycloaddition of epoxides with CO_2. Herein, we would like to disclose an efficient process for the synthesis of cyclic carbonates from epoxides and CO_2 by employing EDTA/TBAB (tetrabutylammonium bromide) as dual-component bifunctional catalyst system. Notably, the catalyst system with EDTA/TBAB worked well for the coupling reactions under mild reaction conditions (5 bar, 70 °C) and cyclic carbonates were gained in good yields and high selectivity.

2. Experimental

2.1. General information

Propylene oxide and epichlorohydrin were purchased from Alfa Aesar, other epoxides and EDTA (ethylenediaminetetraacetic acid), TMEDA (tetramethylethylenediamine), EDTA-3Na (ethylenediaminetetraacetic acid trisodium salt), were of analytical grade and obtained from Aladdin. TBAB, TBAI and KBr were from Tianjin Guangfu Fine Chemical Research Institute. All reagents were used without further purification. Carbon dioxide with a purity of 99.99% was commercially available. The products were characterized by NMR, FT-IR and HRMS. ^1H NMR spectra was recorded on 400 MHz spectrometers using $CDCl_3$ as solvent referenced to $CDCl_3$ (7.26 ppm). ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ (77.00 ppm). Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet and broad singlet. Gas chromatograph (Shimadzu 2014 chromatographer) is equipped with a RTX-5 capillary column (30 m × 0.25 mm) using a flame ionization detector (FID). Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. High-resolution mass spectrometry (HRMS) was conducted using an Ionspec 7.0 T spectrometer.

2.2. General procedure for the cycloaddition reaction of epoxides and CO_2

The cycloaddition reaction of epoxides and CO_2 was conducted in a stainless steel autoclave (50 mL inner volumes). In a typical reaction, the reactor was charged with EDTA (73.1 mg, 0.25 mmol), TBAB (80.6 mg, 0.25 mmol) and styrene oxide (0.6008 g, 5 mmol) successively at room temperature. Then, CO_2 was introduced into the reactor and pressure was adjusted to 5 bar at 70 °C. The autoclave was heated at this temperature for 18 h, and the pressure was kept constant during the reaction. After the reaction was completed, the reactor was cooled to 0 °C in ice-water bath, and then the excess of CO_2 was carefully vented. An aliquot of the sample was taken from the resultant mixture and dissolved in ethyl acetate for ^1H NMR analysis. The conversion of epoxide and yield of cyclic carbonate were determined by 1,3,5-trimethyoxybenzene as the internal standard in $CDCl_3$. The residue was purified by column chromatography with ethyl acetate–petroleum ether as the eluent to afford the desired product. Spectral data for the products (**2a–f**) are as follows:

2.2.1. 4-Phenyl-1,3-dioxolan-2-one (**2a**)

White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.31 (t, ^3J = 8.4 Hz, 1H), 4.78 (t, ^3J = 8.4 Hz, 1H), 5.66 (t, ^3J = 8.0 Hz, 1H), 7.34–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 71.25, 78.09, 125.99, 129.24, 129.74, 135.87, 155.02. IR (KBr): 1779, 1162, 1046, 756, 688 cm^{-1}. HRMS (EI) calc. for [$C_9H_8O_3$]: 164.0473, found: 164.0474.

2.2.2. 4-Methyl-1,3-dioxolan-2-one (**2b**)

Colorless liquid; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.50 (d, ^3J = 6.0 Hz, 3H), 4.04 (t, ^3J = 8.4 Hz, 1H), 4.58 (t, ^3J = 8.4 Hz, 1H), 4.88 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 19.35, 70.71, 73.65, 155.12. IR (KBr): 1791, 1184, 1120, 1076, 1052, 776 cm^{-1}. HRMS (EI) calc. for [$C_4H_6O_3$]: 102.0317, found: 102.0315.

2.2.3. 4-Phenoxymethyl-1,3-dioxolan-2-one (**2c**)

White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.16 (dd, ^3J = 4.4 Hz, ^2J = 10.8 Hz, 1H), 4.24 (dd, ^3J = 3.6 Hz, ^2J = 10.8 Hz, 1H), 4.55 (dd, ^3J = 8.4 Hz, ^2J = 6 Hz, 1H), 4.62 (t, ^3J = 8.4 Hz, 1H), 5.03 (m, 1H), 6.91 (d, ^3J = 8.0 Hz, 2H), 7.02 (t, ^3J = 7.4 Hz, 2H), 7.31 (t, ^3J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 66.26, 66.94, 74.05, 114.66, 122.05,129.72, 157.78. IR (KBr): 2927, 1783, 1600, 1490, 1396, 1161, 1081, 1009 cm^{-1}. HRMS (FAB) calc. for [$C_{10}H_{10}O_4$]: 194.0517, found: 194.0515.

2.2.4. 4-n-Butyl-1,3-dioxolan-2-one (**2d**)

Colorless liquid; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 0.93 (t, ^3J = 7.2 Hz, 3H), 1.26–1.48 (m, 4H), 1.64–1.87 (m, 2H), 4.08 (dd, ^3J = 7.3 Hz, ^2J = 8.0 Hz, 1H), 4.54 (t, ^3J = 8.0 Hz, 1H), 4.68–4.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 13.81, 22.26, 26.44,

Table 1
Catalyst screening for the cycloaddition of CO_2 and SO.[a]

Entry	Catalyst	Co-catalyst	SC yield (%)[b]	Selectivity (%)[b]
1	EDTA	–	0	0
2	–	TBAB	58	98
3	EDTA	TBAB	94	99
4	TMEDA	TBAB	57	95
5	EDTA	TBAI	93	99
6	EDTA	KBr	3	75
7	EDTA-3Na	TBAB	68	96
8[c]	EDTA-3Na	TBAB	78	97
9	Pyrogallol	TBAI	67	99

[a] Unless otherwise specified, the reactions were performed with SO (0.6008 g, 5 mmol), catalyst (0.25 mmol), co-catalyst (0.25 mmol), CO_2 (5 bar), 70 °C, 18 h.

[b] Determined by ^{1}H NMR using 1,3,5-trimethyoxybenzene as an internal standard.

[c] EDTA-3Na (358.2 mg, 1.00 mmol), TBAB (80.6 mg, 0.25 mmol).

33.57, 69.43, 77.07, 155.13. IR (KBr): 2932, 2867, 1785, 1384, 1166, 1058, 774 cm^{-1}. HRMS (FAB) calc. for [$C_7H_{13}O_3$]: 145.0865, found: 145.0866.

2.2.5. 4-i-Propoxy-1,3-dioxolan-2-one (**2e**)

Colorless liquid; ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) 1.16 (d, ^3J = 6.4 Hz, 6H), 3.58–3.70 (m, 3H), 4.38 (dd, ^3J = 8.0 Hz, ^2J = 15.6 Hz, 1H), 4.50 (t, ^3J = 8.0 Hz, 1H), 4.82 (m, 1H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ (ppm) 21.76, 21.87, 66.40, 67.11, 72.86, 75.31, 155.18. IR (KBr): 1787, 1155, 1125, 1084, 1065, 767 cm^{-1}. HRMS (FAB) calc. for [$C_8H_{15}O_4$]: 175.0970, found: 175.0972.

2.2.6. 4-Chloromethyl-1,3-dioxolan-2-one (**2f**)

Colorless liquid; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 3.81 (dd, ^3J = 3.2 Hz, ^2J = 12.0 Hz, 1H), 3.82 (dd, ^3J = 5.2 Hz, ^2J = 12.0 Hz, 1H), 4.43 (dd, ^3J = 6.0 Hz, ^2J = 8.4 Hz, 1H), 4.60 (t, ^3J = 8.4 Hz, 1H), 4.99–5.05 (m, 1H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ (ppm) 43.98, 66.99, 74.43, 154.43. IR (KBr): 1800, 1168, 1112, 1073, 1044 cm^{-1}. HRMS (EI) calc. for [$C_4H_5ClO_3$]: 135.9927, found: 135.9928.

3. Results and discussion

3.1. Catalysts screening

The cycloaddition reaction of styrene oxide (SO) as the model substrate with various catalysts was investigated as depicted in Table 1. No product was detected when only EDTA was used (entry 1). On the other hand, TBAB promoted the cycloaddition to afford styrene carbonate (SC) in a moderate yield (entry 2). Interestingly, combination of EDTA with TBAB as a catalyst rendered SC yield remarkably up to 94% (entry 3). Whereas, a sharp decrease of SC yield was observed (entry 4 *vs.* 3), when EDTA was replaced by no-carboxyl-containing TMEDA (tetramethylethylenediamine, Scheme 2), suggesting carboxylic group presumably activates the epoxide through hydrogen bonding and thus enhances catalytic efficiencies. In addition, the influence of nucleophile and cation was evaluated respectively. Iodide exhibited similar catalytic activity to bromide (entry 3 *vs.* 5). TBAB gave better catalytic activity than KBr (entry 3 *vs.* 6), presumably due to bulkier cation effect on the nucleophilicity of bromide anion and higher solubility associated with TBAB [22]. As a result, the cooperative effect between the carboxyl group as a HBD and halide anion as a nucleophile efficiently promoted the cycloaddition reaction of SO with CO_2. Furthermore, EDTA-3Na bearing one free carboxyl group (Scheme 2) combining with TBAB just gave 68% yield of SC, significantly lower than EDTA/TBAB (entry 7 *vs.* 3). Even if the amount of EDTA-3Na was raised up to fourfold, poorer catalytic performance was found compared with EDTA, albeit with equal mole of free carboxyl (entry 8 *vs.* 3), indicating that the interaction of intramolecular hydrogen bonding is more effective than intermolecular counterpart. Interestingly, EDTA/TBAB showed higher activity than the similar catalyst with activation of CO_2 via single hydrogen bonding in the literature [21], for example, pyrogallol (entry 3 *vs.* 9). Therefore, we concluded that multiple carboxylic groups in one molecule could more effectively activate the epoxide through multi-site hydrogen bonding and thereby greatly enhance catalyst efficiency.

3.2. Variation of reaction parameters

Generally speaking, there are two strategies used to lower the pressure of CO_2 in the cycloaddition reaction. One is to activate CO_2 by employing a strong nucleophile, such as NHC [32]. The other one is to stabilize the reaction intermediate in the ring-opening step. For example, hydroxyl group was used to stabilize the carbonate intermediate through the formation of hydrogen bonding in the reported pyrogallol/TBAB system [21]. In this study, the effect of CO_2 pressure in the EDTA/TBAB catalytic system was illustrated in Table 2. Delightedly, an almost quantitative yield together with excellent selectivity was gained under 5 bar CO_2 (entry 5). Based on previous reports [21,27,28], we assumed that multiple carboxylic groups in EDTA molecule could both activate the substrate, i.e. SO and stabilize the alkoxide intermediate through multi-site hydrogen bonding, thus resulting in enhanced catalytic efficiency at low CO_2 pressure. While further lowering pressure, the yield and selectivity declined to some extent (entries 1–4, Table 2), and the drop in selectivity was speculated that low CO_2 concentration could be favorable for the competitive reactions including the reaction of TBAB with EDTA to the carboxylic ammonia salt and the reaction of TBAB with epoxide to halohydrin, as also observed in Kleij's pyrogallol/TBAI system [33]. It is noteworthy that even with atmospheric pressure of CO_2, SC was retained in 74% yield (entry 1). Moreover, the yield did not have obvious increase under 10 bar CO_2 (entry 6). Accordingly, 5 bar CO_2 was chosen to be a suitable pressure for further study.

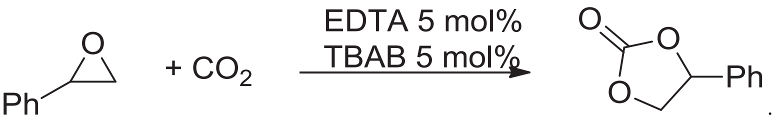
The influence of temperature on the cycloaddition reaction of SO and CO_2 was further examined (entries 5 and 7–12, Table 2). The yield of SC increased sharply from 33% to above 90% when the temperature arose from 40 °C to 80 °C correspondingly (entries 5 and 7–10). Obviously, the reaction was strongly affected by reaction temperature. However, further increasing in the reaction temperature, SC yield decreased dramatically (entries 11, 12), possibly due to the decomposition of EDTA under higher temperature. Therefore, the optimal temperature for the reaction of SC synthesis was 70 °C.

As illustrated in Table 2, the reaction rate was fast during initial 6 h with 78% SC yield (entry 13). However, the reaction proceeded sluggishly to 94% in the next 12 h (entry 5). This may be attributed to the decrease in the reactant concentration and the product accumulation. Further prolonging reaction time only led to a slight rise of SC yield (entry 15). The selectivity of SC fluctuated quite small with above 99% throughout the reaction process.

3.3. Catalytic activity towards other terminal epoxides

To evaluate the utility and generality of the two-component bifunctional catalyst system, the cycloaddition of other terminal epoxides with CO_2 was performed under the optimized reaction conditions. As summarized in Table 3, EDTA/TBAB catalyst system was found to be effective for a variety of terminal epoxides furnishing the corresponding cyclic carbonates **2a–f** in high yields and selectivity. When increasing the steric hindrance, the reactive activity of epoxides slightly declined (entries 1–5, Table 3). In addition, epichlorohydrin showed less activity, which may be ascribed to the electron-withdrawing effect of chloromethyl group (entry 6).

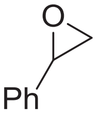
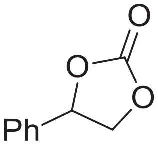
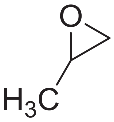
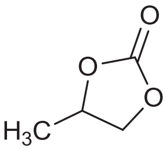
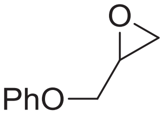
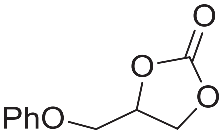
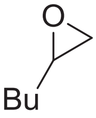
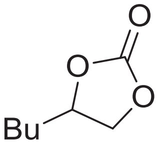
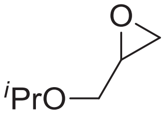
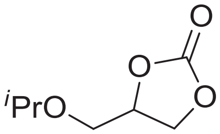
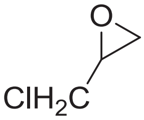
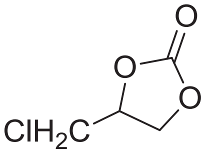
Table 2
Influence of various reaction parameters on the cycloaddition reaction.[a]



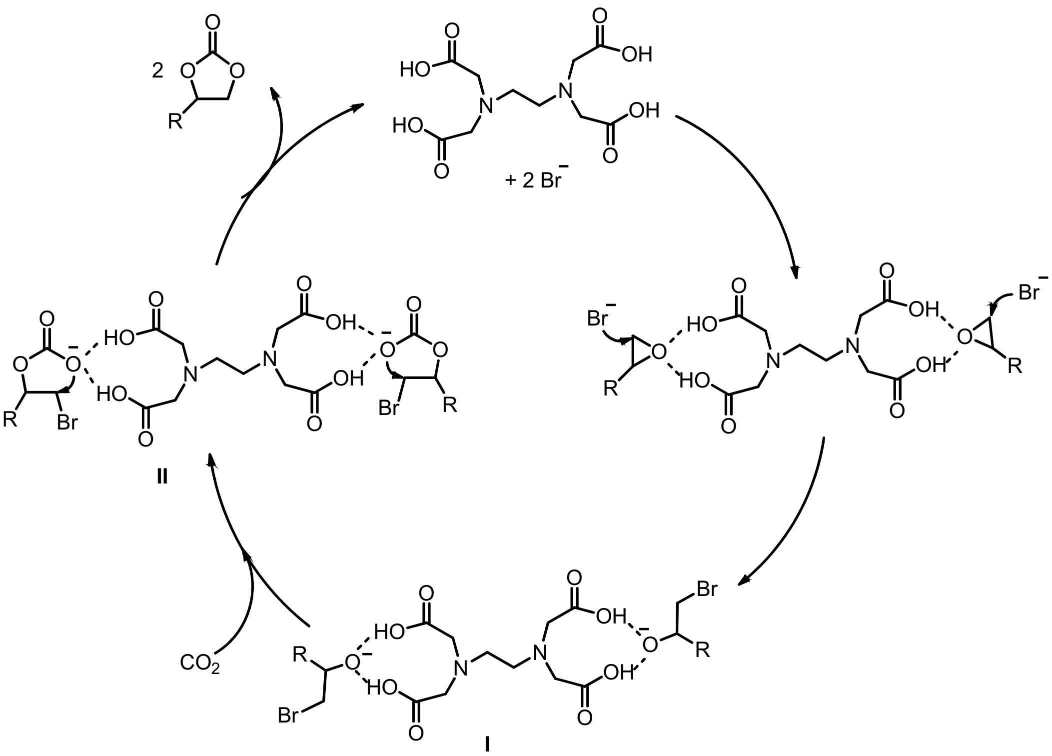
Entry	P (bar)	T (°C)	Time (h)	SC yield (%)[b]	Selectivity (%)[b]
1	1	70	18	74	81
2	2	70	18	79	94
3	3	70	18	82	95
4	4	70	18	86	98
5	5	70	18	94	99
6	10	70	18	98	99
7	5	40	18	33	80
8	5	50	18	40	85
9	5	60	18	82	96
10	5	80	18	95	99
11	5	90	18	88	99
12	5	100	18	78	99
13	5	70	6	78	99
14	5	70	12	87	99
15	5	70	24	99	99

[a] Reaction conditions: SO (0.6008 g, 5 mmol), EDTA (73.1 mg, 0.25 mmol),TBAB (80.6 mg, 0.25 mmol).
[b] Determined by ^{1}H NMR using 1,3,5-trimethyoxybenzene as an internal standard.

Table 3
Various cyclic carbonates synthesis catalyzed by EDTA/TBAB.[a]

Entry	Substrate	Product		Yield (%)[b]	Selectivity (%)[b]
1			**2a**	94	99
2			**2b**	99	99
3			**2c**	98	99
4			**2d**	96	99
5			**2e**	91	98
6			**2f**	90	91

[a] Epoxides (5 mmol), EDTA (73.1 mg, 0.25 mmol), TBAB (80.6 mg, 0.25 mmol), CO_2 (5 bar), 70 °C, 18 h.
[b] Determined by ^{1}H NMR using 1,3,5-trimethyoxybenzene as an internal standard.



Scheme 3. Plausible mechanism for the EDTA/TBAB-catalyzed cycloaddition of CO_2 with epoxides.

3.4. Mechanism

Based on previous mechanistic investigation on cycloaddition reaction [21,28], and the experimental results, the multiple carboxylic groups in one molecule i.e. EDTA are likely able to activate the epoxide through hydrogen bonding interaction, and thereby accelerate the ring-opening step of the epoxide. Consequently, a tentative mechanism for present EDTA/TBAB-catalyzed fixation of CO_2 with epoxides involving with multi-site hydrogen-bonding interaction is illustrated in Scheme 3. Firstly, the carboxylic groups in EDTA interact with the epoxide through multi-site hydrogen bonding. The activated epoxide simultaneously undergoes a ring-opening step upon nucleophilic attack by the bromide from the less sterically hindered β-carbon atom. Meanwhile, the hydrogen bonding-stabilized alkoxide **I** is generated. Then, nucleophilic attack of the intermediate **I** at CO_2 produces the alkyl carbonate anion **II**. Finally, the cyclic carbonate is formed via the intramolecular cyclization with regeneration of the catalyst.

4. Conclusions

In summary, the binary EDTA/TBAB system was proved to be a highly efficient organocatalyst for CO_2 fixation with epoxides to produce cyclic carbonate quantitatively under mild reaction conditions without any additional organic solvent. In particular, synergistic effects of carboxylic groups and bromide anion render the reaction performing smoothly at 5 bar CO_2. In this aspect, multiple carboxylic groups in one molecule i.e. EDTA activate epoxide and stabilize the alkoxide intermediate effectively through multi-site hydrogen bonding in comparison with monocarboxylic acids. Accordingly, the interaction of intramolecular hydrogen bonding is more effective than intermolecular counterpart. The application of EDTA as organocatalyst represents a cost-efficient, eco-friendly and metal-free access to cyclic carbonates. Therefore, this two-component bifunctional catalyst system provides a promising strategy for chemical fixation of CO_2 into valuable compounds and materials. Currently we are designing other types of multi-hydrogen-bonding structures in the context of CO_2 fixation.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.08.062.

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