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Efficient Catalysts *In Situ* Generated from Zinc, Amide and Benzyl Bromide for Epoxide/CO_2 Coupling Reaction at Atmospheric Pressure

Shuai Zhang,*[a,b] Feng Han,[b] Shaorui Yan,[b] Mingyue He, [b] Chengxia Miao,[b] and Liang-Nian He*[a]

Dedication ((optional))

Abstract: Herein, *in situ* generated efficient catalysts were designed for fixation of CO_2 to cyclic carbonates under mild conditions. Zinc bromide and N,N-dibenzyl-N,N-dimethylammonium bromide, being proved as active catalyst species, were *in situ* generated from cheap Zn powder, dimethyl formamide and benzyl bromide, and catalyzed the cycloaddition reaction of CO_2 and various terminal epoxides in moderate to excellent yields at 80 °C and atmospheric pressure of CO_2. The protocol circumvents the preparation of active catalysts, simultaneously possesses good catalytic activity under mild conditions.

Introduction

Carbon dioxide, as a plentiful, low-cost, nontoxic, sustainable C_1 synthon, has gained increasing attention.[1] The chemical CO_2 fixation to value-added commodity chemicals, fuels and materials, nowadays, has been becoming one of research hotspots in both academy and industry.[1] CO_2 has been utilized in both the synthesis of organic carbonate, various important heterocycles, and the reduction to methanol, formic acid and so on. In the pursuit of the CO_2-based products, the coupling reaction of CO_2 and epoxides to afford cyclic carbonates (Scheme 1),[2] one of the few commercial routes with CO_2 as a raw material, is of great importance and has been a hot topic in catalysis, being ascribed to the unique properties of cyclic carbonate. Organic carbonates have been widely used as excellent high-boiling polar aprotic solvents, important intermediates in the production of pharmaceuticals and electrolytic elements of lithium secondary batteries.[2] In the past decades, numerous homogeneous and heterogeneous catalysts have been well developed by many research groups for efficient synthesis of cyclic carbonates, including metal oxides, (transition) metal complexes,[3a-e] alkali metal salts,[3f-g] ionic liquids,[3h] organocatalysts[3i] and so on. Furthermore, the application of a metal complex in conjunction with a halide anion as a nucleophile usually shows excellent catalytic efficiency. The halide anion can be incorporated in the metal complex or added into catalytic system. Kleij group developed aluminum-aminotriphenolate complexes with tetrabutylammonium iodine as co-catalyst, which showed excellent catalytic activity.[4] Ema and coworkers synthesized bifunctional Mg^{II} porphyrin catalysts bearing eight tetraalkylammonium bromide groups with alkyl chain, which presented high catalytic activity (turnover frequency, 19,000 h^{-1}).[5] Bifunctional polymers by combining imidazolium-based ionic liquids with zinc(II) porphyrin were designed by Ji group, and exhibited good catalytic performance and excellent recyclability. [6]

Despite of great achievements, examples of active metal catalyst *in situ* generated from commonly available reagents with simple synthetic process are limited. Development of active catalysts through simple strategies from cheap, easily-obtained, low-toxic materials under mild conditions is still desirable. The integration of catalyst formation and subsequent catalysis is dependent on the rational design of efficient catalyst and its compatibility with the reaction system. Hirose group employed iminium salts *in situ* generated from benzyl bromide (BnBr) and N,N-dimethylformamide (DMF) for the coupling of CO_2 and epoxide at 120 °C, 1 bar CO_2.[7] Our group described *in situ* generated $ZnCl_2(TBD)_2$ complex (TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene) acted as a robust catalyst for the carboxylative cyclization of propargylic amines with CO_2 without pre-preparation and further isolation.[8]

Zinc, presenting high natural abundance and low environmental impact, has found wide application in the field of CO_2 utilization for the past decades.[9] For the cycloaddition reaction, a series of zinc salts/ionic liquid binary catalysts, such as $ZnCl_2$/[BMIm]Br,[7a-b] $ZnBr_2$/*n*-Bu_4NI,[7c] $Zn(OPO)_2$/*n*-Bu_4NI,[7d] $Zn_4(OCOCF_3)_6O$/*n*-Bu_4NI,[7e] have been developed, and their high catalytic efficiency presumably is ascribed to that the effective activation of epoxide by the Lewis acidic Zn^{2+} cation facilitates the ring-opening at the less substituted C-O bond upon nucleophilic attack by halide anion.[10]

Herein, we envisioned that active binary catalysts could be *in situ* generated from Zn powder, DMF and BnBr. Iminium salts generated from BnBr and DMF[7] would be reduced[11] and hydrolysed in presence of zinc powder and trace water, to provide $ZnBr_2$ and N,N-dibenzyl-N,N-dimethylammonium bromide ([DBDMA]Br). $ZnBr_2$/[DBDMA]Br binary catalysts containing a Lewis acidic center and a Brønsted basic center, were *in situ* generated from Zn powder, DMF and BnBr, and served as active catalysts in one pot for the cycloaddition reaction of CO_2 and epoxide at 80 °C and atmospheric pressure of CO_2 (Scheme 1).

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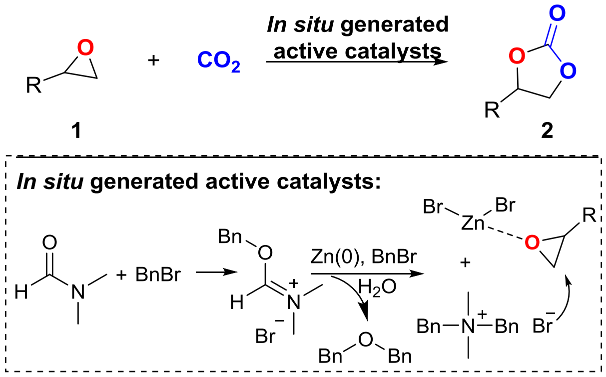
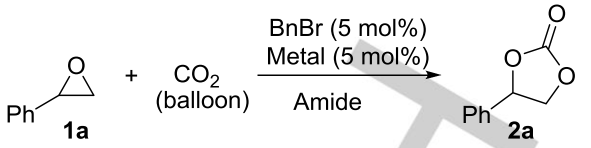


Scheme 1. *In situ* generated active catalysts for the cycloaddition reaction of epoxide and CO_2.

Results and Discussion

Initially, styrene oxide (**1a**) was chosen as model substrate for the cycloaddition reaction at 80 °C and atmospheric CO_2 pressure, and Zn powder, DMF and BnBr were selected as raw materials to generate the proposed binary catalysts. As summarized in Table 1, in the absence of Zn, DMF or BnBr respectively, almost no product was observed with no obvious conversion of **1a** (entries 1-3), indicating no active catalysts were generated. Inspiringly, the combination of Zn powder/DMF/BnBr resulted in excellent yield (97%, entry 4), suggesting active catalysts were generated and catalyzed the cycloaddition reaction. Subsequently, the effects of Zn, DMF and BnBr were investigated respectively. The replacement of DMF by DMAc and DEAc provided the corresponding carbonate **2a** with relatively lower yields albeit with good selectivity (entries 5-6). However, the application of DMSO resulted in significantly reduced selectivity (39%, entry 7). Interestingly, the employment of anhydrous DMF led to reduced yield (74%, entry 8), and a retention of high yields was observed by adding 5, 10 mol% distilled water into the reaction system (entries 9, 10), indicating that moisture probably was involved in the generation of active catalysts. Taking into consideration that polar DMF as solvent probably enhanced the reactivity, $CHCl_3$ instead of DMF was used employed, which resulted in lower yield (22%, entry 11). It indicates that DMF promotes the cycloaddition mainly by facilitating the generation of active catalysts. The employment of newly activated Zn powder gave similar yield (95%, entry 12) with that of non-activated powder. Therefore, non-activated Zn powder was used in the following experiments. On the other hand, the alternative of metal (such as Mn, Mg, Fe, Al) or BnBr in this cycloaddition reaction gave an adverse effect (entries 13-18). The employment of Zn powder delivered excellent yield (97%, entry 4), while Mn, Mg, Fe resulted in poor yields (entries 13-15), and Al powder gave poor selectivity (entry 16). These results are probably attributed to that no corresponding active intermediates were generated according to the proposed pathway, proving the subtlety of this catalytic system. When BnBr was replaced by relatively less active benzyl chloride and 1-(chloromethyl)-4-nitrobenzene (entries 17-18), all the reactants were recovered, indicating no generation of any active catalysts.

Table 1. Catalytic cycloaddition of CO_2 with **1a** by Zn powder/BnBr/amide.[a]



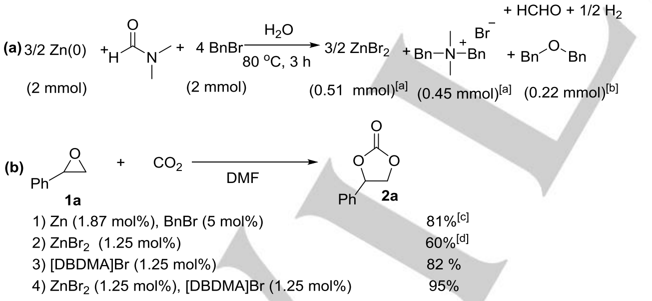
Entry	Metal	Amide	Conv. (%)	Yield (%)
1	---	DMF	4	4
2	Zn	---	<1	0
3[b]	Zn	DMF	<1	0
4	Zn	DMF	>99	97
5	Zn	DMAc	75	74
6[c]	Zn	DEAc	44	43
7	Zn	DMSO	>99	39
8[d]	Zn	DMF	78	74
9[e]	Zn	DMF	94	93
10[f]	Zn	DMF	93	92
11[g]	Zn	DMF	85	22
12[g]	Zn	DMF	>99	95
13	Mn	DMF	34	34
14	Mg	DMF	23	18
15	Fe	DMF	40	34
16	Al	DMF	93	54
17[i]	Zn	DMF	<1	0
18[j]	Zn	DMF	<1	0

[a] Reaction conditions: **1a** (5 mmol, 601.5 mg), metal powder (0.25 mmol, 5 mol%), amide (500 mg), BnBr (42.8 mg, 0.25 mmol, 5 mol%), CO_2 balloon, 80 °C, 12 h; the conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard. [b] Without BnBr. [c] DEAc = diethylacetamide. [d] Anhydrous DMF. [e] Distilled water 4.5 g, 5 mol%. [f] Distilled water 9.0 g, 10 mol%. [g] DMF (0.25 mmol, 5 mol%), $CHCl_3$ (500 mg) as solvent. [h] Activatted Zn powder. [i] Benzyl chloride (31.6 mg, 5 mol%) instead of BnBr. [j] 1-(Chloromethyl)-4-nitrobenzene (42.9 mg, 5 mol%) instead of BnBr.

In situ FTIR (Fourier Transform Infrared Spectroscopy) under 1 bar of CO_2 pressure was also performed to gain insight into the cycloaddition reaction. Figure 1 explicitly shows the peak change with reaction time. Initially, almost no epoxide was consumed in 1.5 h, and slight decrease of peaks at 1094 and 1388 cm^{-1} belonging to the absorption of DMF was observed during the 1.5 h, which probably was ascribed to the process of *in situ* generation of active catalysts. Subsequently, absorption peak of the carbonyl group at 1806 cm^{-1} increased gradually, indicating the beginning of the cycloaddition reaction. The weakening of the signal at 875 cm^{-1} (benzene skeleton vibration) of **1a** was accompanied with the increasing peaks at 1164 and 1068 cm^{-1} (C-O stretching vibration) of **2a**, suggesting the smooth running of the cycloaddition process.

To provide further evidences to support the proposed *in situ* generation of active catalysts, control reactions involving Zn powder/DMF/BnBr were performed to obtain the proposed $ZnBr_2$ and tetraalkylammonium bromide. Expectedly, as shown in Scheme 2a, $ZnBr_2$, [DBDMA]Br and dibenzyl ether were generated and isolated by column chromatography. Peaks at 2θ = 13.64°, 21.25°, 25.98°, 27.50°, 28.24°, 31.31°, 35.02°, 46.04° in the XRD (X-ray powder diffraction) spectrum (Figure S1) are ascribed to $ZnBr_2$ (JCPDS #No. 36-0756). [DBDMA]Br and dibenzyl ether were characterized by NMR (nuclear magnetic resonance) spectra. As shown in Scheme 2a, excessive Zn powder was used, which was agreement with that residue Zn powder was found after the experiments. As shown in Scheme 2a, to convert one mol BnBr completely, 3/8 mol Zn powder would be consumed. If using this stoichiometry for the conversion of **1a** (Zn 1.87 mol%, BnBr 5 mol%), 81% yield of **2a** was obtained with 83% conversion (Scheme 2b). Therefore, to promote the generation of active catalysts, 5 mol% Zn powder was used in the cycloaddition reaction. According to Scheme 2a, the amount of $ZnBr_2$ and [DBDMA]Br generated in the cycloaddition reaction were calculated to be approximately 1.25 mol%, which whereafter was used in Scheme 2b. Although pure $ZnBr_2$ or [DBDMA]Br (1.25 mol%) as sole catalyst could also catalyze the cycloaddition reaction, the relative lower yield (60%, 82%, respectively) suggests that $ZnBr_2$ or [DBDMA]Br alone is not the real catalyst. The combination of $ZnBr_2$ and [DBDMA]Br gave high yield (95%), which was consistent with the results in Table 1. Therefore, based on these results above, $ZnBr_2$/[DBDMA]Br was *in situ* generated and served as the real, active catalysts for the coupling reaction of **1a** and CO_2.

To survey the applicability of this *in situ* generated active catalysts, various functionalized terminal epoxides were tested at atmospheric CO_2 pressure, 80 °C. As listed in Scheme 3, a series of epoxides were smoothly converted to the corresponding cyclic carbonates (**2a–h)** in excellent yields (up to 99%). Interestingly, probably being ascribed to the steric effect, isobutylene carbonate **2i** exhibited relatively lower yield even under harsh conditions.



Scheme 2. Control experiments. (a) Zn powder (130.6 mg, 2 mmol), BnBr (342.1 mg, 2 mmol), DMF (500 mg), 80 °C, 12 h. (b) **1a** (601.5 mg, 5 mmol), DMF 500 mg, 80 °C, 12 h, CO_2 (balloon). [a] Isolated yield. [b] Determined by GC using diphenyl as an internal standard. [c] 83% conversion. [d] 96% conversion of **1a.**

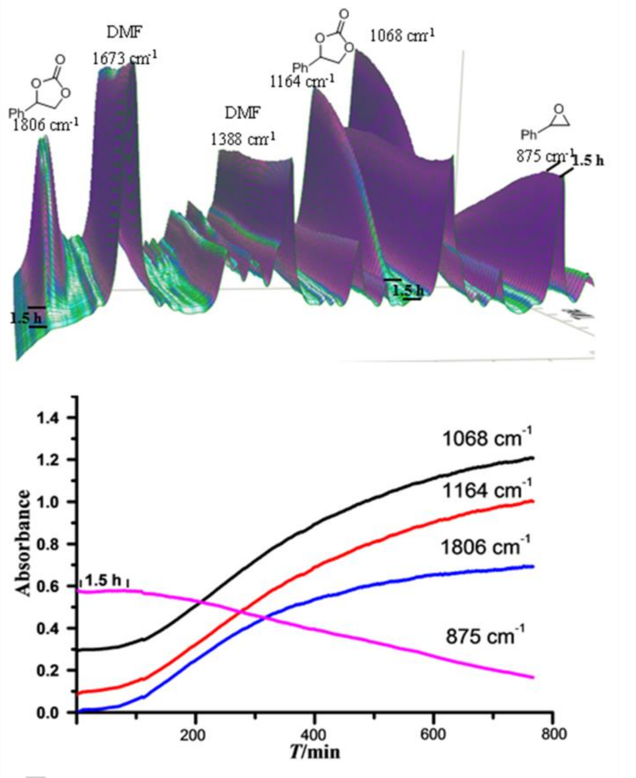
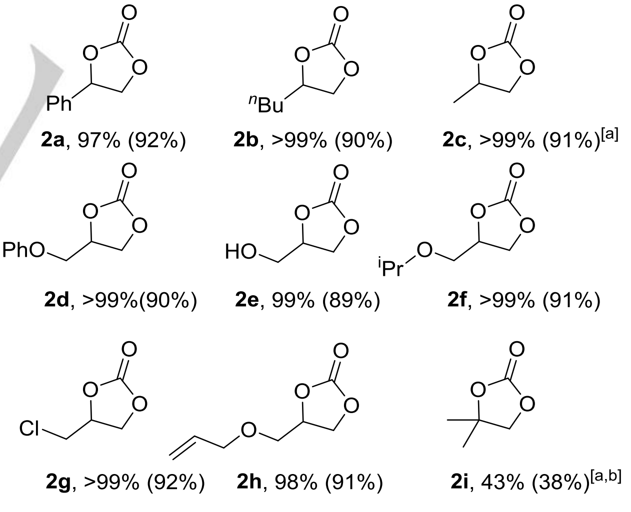
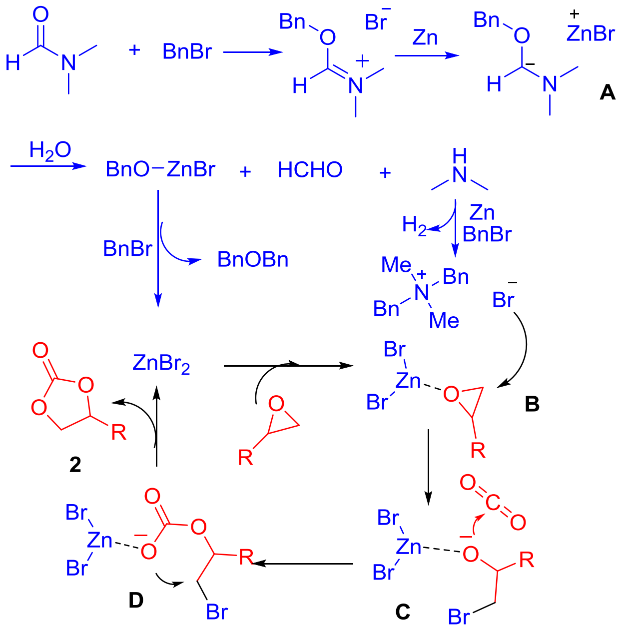


Figure 1. *In situ* FTIR spectra for the coupling reaction. **1a** (2.40 g, 20 mmol), Zn powder (65.4 mg, 5 mol%), DMF (1.50 g), BnBr (171.0 mg, 5 mol%), 80 °C, CO_2 (balloon).



Scheme 3. Substrate scope. Unless otherwise stated, the reactions were carried out with 5.0 mmol substrate in the presence of DMF (500 mg), BnBr (42.8 mg, 0.25 mmol), Zn powder (16.3 mg, 0.25 mmol) at 80 °C, CO_2 (balloon), 12 h; yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard; isolated yields were listed in brackets. [a] 25 mL stainless-steel autoclave equipped with an inner glass tube, 0.5 MPa CO_2. [b] 120 °C.



Scheme 4. Proposed mechanism of the generation of catalysts and the cycloaddition reaction.

Accordingly, based on these results and previous reports, two successive processes were proposed in this reaction, including the generation of active catalysts and the cycloaddition (Scheme 4). Initially, DMF interacted with BnBr to generate iminium salt **A**.[7] The resulting iminium salts **A** was then reduced through umpolung conversion reaction by way of two-electron transfer in the presence of Zn powder to generate complex **B**.[12] The complex B was highly reactive, and could be rapidly hydrolysed to generate benzyloxy zinc bromide, formaldehyde and dimethylamine, and immediately convert to $ZnBr_2$ and [DBDMA]Br in the presence of BnBr.[11,13] Subsequently, the generated binary $ZnBr_2$/[DBDMA]Br catalyzed the coupling reaction, which initiated with the interaction of oxygen atom in epoxide with Lewis acidic Zn^{2+} center in $ZnBr_2$ (**C**), facilitating the ring-opening by nucleophilic attack of Br anion of [DBDMA]Br to generate an alcoholate **D**. Then CO_2 was introduced to form the intermediate **E** followed by an intramolecular cyclization to obtain the targeted compounds with the regeneration of $ZnBr_2$/[DBDMA]Br.

Conclusions

In summary, efficient binary catalysts originating from Zn powder, DMF and BnBr were developed for CO_2 fixation. Active binary $ZnBr_2$ and [DBDMA]Br, were *in situ* generated, and presented good compatibility and high catalytic activity for the coupling reaction of epoxide and CO_2. Various cyclic carbonates were obtained in this catalytic system with good yields at 80 ^{o}C and 1 bar CO_2. These results achieved mark this protocol as a promising motif of rational design of *in situ* active catalysts from simple raw materials for the synthesis of organic carbonate starting from CO_2.

Experimental Section

General

Propylene oxide were purchased from Alfa Aesar, other epoxides, BnBr, benzyl chloride, 1-(chloromethyl)-4-nitrobenzene and anhydrous DMF were of analytical grade and obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD. DMF, DMAc, DEAc, DMSO and metal powders were purchased from Tianjin Guangfu Fine Chemical Research Institute. All reagents were used without further purification. Carbon dioxide with a purity of 99.9% was commercially available. Activated Zn powder was obtained according to reference 14. The products were characterized by NMR spectra. ^{1}H NMR spectra were recorded on 400 MHz spectrometers using $CDCl_3$ as solvents referenced to $CDCl_3$ (7.26 ppm). ^{13}C NMR spectra were recorded at 100.6 MHz in $CDCl_3$ (77.16 ppm). Gas chromatograph (Shimadzu 2014 chromatographer) is equipped with a RTX-50 capillary column (30 m × 0.25 mm) using a flame ionization detector (FID). *In situ* FTIR spectra were collected on a Mettler Toledo React IR ic10, Diamond ATR probe, by using an ic IR analysis system. The probe was placed in the middle of the mixture, which was constantly stirred magnetically, and the spectra were collected *in situ* during the cycloaddition reaction. ESI-MS was recorded on an LCQ-Advantage instrument from Thermo-Finnigan.

General procedure for the cycloaddition reaction of epoxide with CO_2

The cycloaddition reaction of epoxide and CO_2 was conducted in a 10 mL Schlenk flask. In a typical reaction, the flask was charged with Zn powder (16.3 mg, 0.25 mmol), BnBr (42.8 mg, 0.25 mmol), DMF (500 mg), and epoxides (0.50 mmol) successively at room temperature. The flask was capped with a stopper and sealed. Then, the reaction mixture was stirred at 80 °C for 12 h under an atmosphere of CO_2 (1.5 L-balloon). After the reaction was completed, the mixture was cooled to room temperature and 1,3,5-trimethoxybenzene as internal standard was added. The conversion of epoxides and yield of cyclic carbonates were determined by ^{1}H NMR in $CDCl_3$. Then, the residue was further purified by column chromatography (silica gel as stationary phase) with ethyl acetate-petroleum ether as the eluent to afford product. All cyclic carbonates **2a-i** have been reported previously and the characterization data are all in good agreement with literature value.[10d]

4-Phenyl-1,3-dioxolan-2-one (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.30 (m, 5H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.33 (t, *J* = 8.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 155.02, 135.87, 129.74, 129.24, 125.99, 78.09, 77.55, 77.23, 76.91, 71.25.

4-*n*-Butyl-1,3-dioxolan-2-one (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (tt, *J* = 7.5, 3.8 Hz, 1H), 4.54 (t, *J* = 8.1 Hz, 1H), 4.08 (dd, *J* = 8.4, 7.2 Hz, 1H), 1.92-1.78 (m, 1H), 1.70 (dd, *J* = 7.0, 2.9 Hz, 1H), 1.39 (dd, J = 8.7, 2.2 Hz, 4H), 0.93 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 155.13, 77.07, 69.43, 33.57, 26.44, 22.26, 13.81.

4-Methyl-1,3-dioxolan-2-one (2c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03-4.79 (m, 1H), 4.59 (dt, *J* = 7.9, 5.3 Hz, 1H), 4.17-3.91 (m, 1H), 1.49 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 155.16, 73.71, 70.72, 19.28.

4-Phenoxymethyl-1,3-dioxolan-2-one (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (t, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 5.09-4.95 (m, 1H), 4.62 (t, *J* = 8.4 Hz, 1H), 4.54 (dd, *J* = 8.5, 5.9 Hz, 1H), 4.24 (dd, *J* = 10.5, 4.4 Hz, 1H), 4.16 (dd, *J* = 10.5, 3.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 129.72, 122.05, 114.66, 74.05, 66.94, 66.26.

4-(Hydroxymethyl)-1,3-dioxolan-2-one (2e): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.75-4.85 (m, 1H), 4.45-4.55 (m, 2H), 3.97 (d, 1H), 3.71 (d, 1H), 2.50-3.00 (br, 1H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 155.58, 76.79, 65.92, 61.75.

4-*i*-Propoxy-1,3-dioxolan-2-one (2f): ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.82 (m, 1H), 4.50 (t, J = 8.0 Hz, 1H), 4.38 (dd, J = 8.0 Hz, J= 15.6 Hz, 1H), 3.58-3.70 (m, 3H), 1.16 (d, J = 6.4 Hz, 6H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 155.18, 75.31, 72.86, 67.11, 66.40, 21.87, 21.76.

4-Chloromethyl-1,3-dioxolan-2-one (2g): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.99-5.05 (m, 1H), 4.60 (t, J = 8.4 Hz, 1H), 4.43 (dd, J = 6.0 Hz, 8.4 Hz, 1H), 3.82 (dd, J = 5.2 Hz, 12.0 Hz, 1H), 3.81 (dd, J = 3.2 Hz, 12.0 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 154.43, 74.43, 66.99, 43.98.

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (2h): ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.61-3.72 (m, 2H), 4.06-4.07 (m, 2H), 4.39-4.43 (m, 1H), 4.51 (t, 1H), 4.80-4.86 (m, 1H), 5.22-5.32 (m, 2H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 155.03, 133.76, 118.11, 75.11, 72.74, 68.95, 66.41.

4,4-Dimethyl-1,3-dioxolan-2-one (2i): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.17 (s, 2H), 1.53 (s, 6H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 154.65, 81.76, 75.39, 25.98.

Synthesis and characterization of [DBDMA]Br, ZnBr$_2$ and dibenzyl ether

In a 10 mL Schlenk flask, Zn powder (65.3 mg, 1 mmol), benzyl bromide (342.1 mg, 2 mmol) and DMF (500 mg) were charged successively at room temperature. The flask was capped with a stopper and sealed. Then, the reaction mixture was stirred at 80 °C for 3 h. After the reaction was completed, the mixture was purified by column chromatography (silica gel as stationary phase) with ethyl acetate-petroleum ether (1:5) as the eluent to afford dibenzyl ether (0.22 mmol), and with ethanol as the eluent to afford [DBDMA]Br and ZnBr$_2$ mixture. After removing ethanol and adding 1 mL dichloromethane, ZnBr$_2$ (white solid, 0.51 mmol) could be precipitated out and filtered. And [DBDMA]Br (white solid, 117.0 mg, 0.45 mmol) was obtained by evaporating the dichloromethane solution. ZnBr$_2$ was characterized by X-ray powder diffraction (Figure S1, JCPDS #No. 36-0756). The characterization data of dibenzyl ether and [DBDMA]Br are all in good agreement with literature value.[15,11]

Dibenzyl ether: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (d, 8H), 7.26-7.31 (m, 2H), 4.70 (s, 4H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 140.99, 128.72, 127.82, 127.13, 65.54.[15]

[DBDMA]Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (m, 4H), 7.44 (m, 6H), 5.18 (s, 4H), 3.14 (s, 6H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 133.54, 130.93, 129.39, 127.34, 67.88, 48.41. HRMS (ESI): m/z: calcd for $C_{16}H_{20}BrN$: 305.0779, $[M\text{-}Br]^+$; found 226.1593.[11]

Acknowledgements ((optional))

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Keywords: carbon dioxide fixation • C1 building blocks • atmospheric pressure • cyclic carbonates• Zinc

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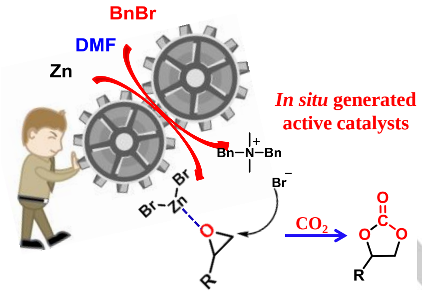
Key Topic: CO_2 Fixation

FULL PAPER

Active catalysts *in situ* generated from Zn powder, dimethyl formamide and benzyl bromide were designed for fixation of CO_2 to cyclic carbonates at 80 °C and atmospheric pressure of CO_2. Zinc bromide and N,N-dibenzyl-N,N-dimethylammonium bromide, being proved as active catalyst species, were *in situ* generated and immediately converted various terminal epoxides to the corresponding carbonates efficiently.



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Page No. – Page No.

Efficient Catalysts *In Situ* Generated from Zinc, Amide and Benzyl Bromide for Epoxide/CO_2 Coupling Reaction at Atmospheric Pressure