

Highly active, hexabutylguanidinium salt/zinc bromide binary catalyst for the coupling reaction of carbon dioxide and epoxides

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Abstract

An experimentally simple and inexpensive catalyst system based on hexabutylguanidinium/ZnBr₂ has been developed for the coupling of carbon dioxide and epoxides to form cyclic carbonates with significant catalytic activity under mild reaction conditions without using additional organic solvents (e.g. the turnover frequencies (TOF, h⁻¹) values as high as 6.6 × 10³ h⁻¹ for styrene oxide and 1.01 × 10⁴ h⁻¹ for epichlorohydrin). This catalyst system also offers the advantages of recyclability and reusability. Therefore, it is a very effective, environmentally benign, and simple catalytic process. The special steric and electrophilic characteristics of hexabutylguanidinium bromide ionic liquid result in the prominent performance of this novel catalyst system.

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Keywords: Hexabutylguanidinium salts; Zinc bromide; Ionic liquid; Epoxides; Carbon dioxide; Cyclic carbonate

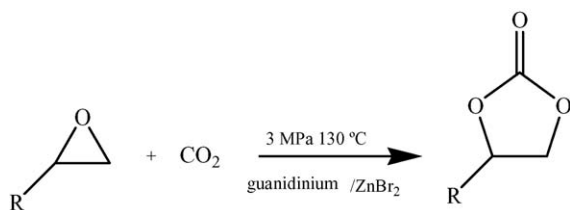
1. Introduction

The formation of cyclic carbonates via cycloaddition of epoxides and carbon dioxide is one of the routes for chemical fixation of CO₂, which has received much attention, since the cyclic carbonates showed interesting applications as polar aprotic solvents, precursors for polycarbonate materials, and intermediates in organic synthesis (Scheme 1) [1]. Although numerous catalyst systems have been developed for this transformation [2], they normally suffered from drawbacks of one kind or another, such as the low catalyst stability or activity, air sensitivity, the need for co-solvent or co-catalyst, and the requirement for high pressures and/or high temperatures. Hence the exploration of highly efficient, easy separation and recycling of the catalyst system for this transformation under mild conditions still remains a challenge.

In recent years, ionic liquids have received considerable interest due to their unique advantages of high thermal stability, negligible vapor pressure, diversity, recyclability, and immis-

cibility with a number of organic solvents [3]. Many catalyst systems based on ionic liquids have been successfully developed for the cycloaddition between epoxides and carbon dioxide, in which moderate yields or TOF values were obtained (in some cases, the supercritical conditions were needed) [4]. Recently, we directed our efforts to optimize the structure of ionic liquids to improve their catalytic activity for this transformation, and we found that hexabutylguanidinium ionic liquids were more effective than the imidazolium salt analogues [5]. Due to the great interest in this topic, herein, we report a novel catalyst system consisting of hexabutylguanidinium salt ionic liquids and ZnBr₂ for chemical fixation of CO₂ onto epoxides. This catalyst system has high catalytic activity (e.g. TOF values as high as 6.6 × 10³ h⁻¹ for the cycloaddition between CO₂ and relatively unreactive styrene oxide and 1.01 × 10⁴ h⁻¹ for epichlorohydrin), and it also offers the advantages of recyclability and reusability. Therefore, it is a very effective, environmentally benign, and simple catalytic process. At the same time, our present study demonstrates that the hexaalkylguanidinium salts should be more suitable as co-catalysts during similar Lewis acid–base catalyst systems for this transformation than the quaternary ammonium salts, pyridinium salts, and imidazolium salts used commonly today.

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Scheme 1.

2. Experimental and methods

GC analysis was carried out on a Hewlett-Packard III 5720 instrument; ^1H NMR was determined on a Bruker spectrometer (300 MHz) with TMS as internal standard; all the epoxides were used after distillation over CaH_2 .

2.1. Synthesis of hexaalkylguanidinium salts

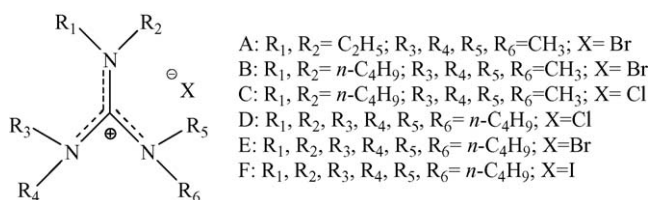
The hexaalkylguanidinium salts were prepared according to the literature (Scheme 2) [5,6].

2.2. Coupling reaction of epoxides and carbon dioxide

All cycloaddition reactions were performed in a 100 ml stainless steel autoclave equipped with a mechanic stirrer. For a typical reaction, hexabutylguanidinium bromide (0.0572 g, 0.00012 mol), ZnBr_2 (0.0045 g, 0.00002 mol) and propylene oxide (15 ml, 0.215 mol) were successively charged into the reactor without using any additional solvent. The reactor vessel was placed under a constant pressure of carbon dioxide for 5 min to allow the system to equilibrate and then heated to 130°C for 1 h. After cooling to ambient temperature, the resulting product mixture was transferred to a 50 ml round bottom flask. Firstly, unreacted propylene oxide was removed in vacuo, and then the product propylene carbonate was obtained as a colorless liquid. All the cyclic carbonates were identified by GC and 300 MHz NMR. For the recycling process, after the propylene carbonate was removed by distillation, the remaining catalyst was reused for further reaction with a fresh charge of propylene oxide by the same procedure as performed by the initial reaction.

3. Results and discussion

Recently, Sun et al. [7] reported that ZnBr_2 was more suitable as Lewis acid catalyst than FeBr_3 , ZnCl_2 , and ZnI_2 , and so on, in this transformation. Furthermore, ZnBr_2 was very cheap, so we used ZnBr_2 as the model Lewis acid catalyst in our present work.



Scheme 2.

3.1. The effect of reaction parameters on cycloaddition of CO_2 to propylene oxide

In order to investigate the effect of the structure of the co-catalyst on the catalytic activity of this catalyst system, several co-catalysts were used in our experiments, including tetrabutylammonium bromide, butylpyridinium bromide (BuPyBr), 1-methyl-3-butyl-imidazolium bromide (BMImBr) and hexaalkylguanidinium salts (Scheme 2). The catalytic activities of zinc bromide in conjunction with various co-catalysts and various molar ratio of co-catalyst to zinc bromide were evaluated for the coupling reaction of carbon dioxide and propylene oxide (PO), and the results are listed in Table 1. From Table 1, it can be seen that all catalyst systems using different co-catalysts exhibit good catalytic activity (entries, 1–9). Among these co-catalysts, the hexaalkylguanidinium salts exhibit higher catalytic activity than the others used in this study, and the hexabutylguanidinium bromide is the most effective co-catalyst. Furthermore, the catalytic activity of hexaalkylguanidinium salts is sensitive to their bulkiness of cations, i.e. the order of activity is E, D, F, >B, C > A, in accordance with the order of the size of the guanidinium salt cation. It is noteworthy that the catalytic activity is greatly influenced by the halide anion of the ionic liquids, and the results suggest that the activity decreased in the order $\text{Br}^- > \text{I}^- > \text{Cl}^-$ (entries, 7–9), which could be caused by the cooperation of the moderate nucleophilicity and high leaving ability of Br^- ion.

Table 1 also shows that low yields are obtained when hexabutylguanidinium salt alone was used as catalyst under these conditions while ZnBr_2 itself does not catalyze the reaction (entries 10, 14). In combination of zinc bromide with hexabutylguanidinium ionic liquids, the novel catalyst system exhibits a significantly highly catalytic activity for this coupling reac-

Table 1

Effects of the structure of the co-catalyst and the molar ratio of co-catalysts to ZnBr_2 on the coupling reaction of carbon dioxide and propylene oxide (PO) to form propylene carbonate^a

Entry	Catalyst system	The molar ratio ^b	Yield (%) ^c	TOF (h^{-1}) ^d
1	<i>n</i> -Bu ₄ NBr/ ZnBr_2	2:1	40	1440
2	BuPyBr/ ZnBr_2	2:1	39	1410
3	BMImBr/ ZnBr_2	2:1	46	1650
4	A/ ZnBr_2	2:1	59	2050
5	B/ ZnBr_2	2:1	63	2208
6	C/ ZnBr_2	2:1	57	2005
7	D/ ZnBr_2	2:1	52	1875
8	F/ ZnBr_2	2:1	58	2087
9	E/ ZnBr_2	2:1	71	2524
10	E	1:0 ^e	18	–
11	E/ ZnBr_2	4:1	81	2878
12	E/ ZnBr_2	6:1	94	3355
13	E/ ZnBr_2	8:1	100	3571
14	ZnBr_2	0:1 ^f	Trace	–

^a Reaction conditions: ZnBr_2 : (0.00004 mol); propylene oxide (PO) (10 ml, 0.143 mol); time: 1 h; temperature: 100°C ; initial CO_2 pressure: 4.0 MPa.

^b The molar ratio of guanidinium ionic liquids to ZnBr_2 .

^c Isolated yield, the selectivity >99%.

^d Moles of propylene carbonate produced per mole of catalyst per hour.

^e Hexabutylguanidinium bromide 0.038 g and without ZnBr_2 .

^f Without ionic liquid.

Table 2
Effects of temperatures and pressures of carbon dioxide^a

Entry	Temperature (°C)	Pressure (MPa)	Yield (%) ^b	TOF ^c
1	100	3.0	55	5904
2	100	2.0	43	4610
3	100	4.0	31	3355
4	90	3.0	23	2439
5	110	3.0	57	6100
6	120	3.0	61	6586
7	130	3.0	80	8566
8	140	3.0	81	8670

^a Reaction condition: propylene oxide (PO) (15 ml, 0.215 mol); ZnBr₂: (0.00002 mol); catalyst system: E/ZnBr₂ = 6:1; time: 1 h.

^b Isolated yield, the selectivity >99%.

^c Moles propylene carbonate produced per mole of catalyst per hour.

tion (Table 1, entries 4–9, 11–13). We also find that the yield of propylene carbonate increases with increasing molar ratio of guanidinium to zinc bromide (entries 9–14). However, increasing molar ratio from 6:1 to 8:1 resulted in only slight improvements in the yield. Therefore, we consider that the best molar ratio of guanidinium to zinc bromide is 6:1 in this reaction.

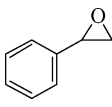
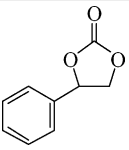
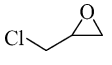
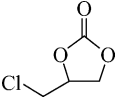
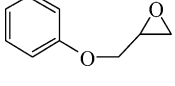
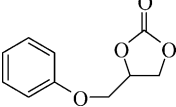
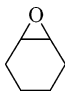
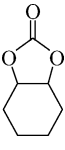
Besides these conditions, we also investigated the effect of reaction temperatures and carbon dioxide pressures on this reaction. We carried out the coupling reaction of propylene oxide and carbon dioxide under different reaction temperatures and carbon dioxide pressures. From the results shown in Table 2, we find that when the reaction is carried out at various CO₂ initial pressures at 100 °C, the highest catalytic activity is attained at 3.0 MPa CO₂ pressure. Increasing or decreasing the CO₂ pressure from

3.0 MPa results in a decrease in activity (entries 1–3). A possible reason is that excessive CO₂ pressure may retard the interaction between propylene oxide and the catalyst, thus resulting in low catalytic activity [2]. As shown in Table 2 (entries 4–8), the catalytic activity of the catalyst system is pretty sensitive to reaction temperatures. The yields of propylene carbonate increase with increasing reaction temperatures when the reaction is concluded at different reaction temperatures. However, the enhancement of the reaction temperature from 130 to 140 °C results in only slight increases in activity. From the results mentioned above, we conclude that the optimum reaction temperature and CO₂ pressure in this catalytic process is 130 °C and 3.0 MPa, respectively.

3.2. The cycloaddition of CO₂ with epoxides to give cyclic carbonates

Under the optimum reaction conditions, a series of terminal epoxides were examined for the synthesis of corresponding cyclic carbonates. From the results summarized in Table 3, we conclude that this catalyst system exhibits high efficiency for almost all of the mono-substituted terminal epoxides (entries 1–3). It is worth noting that this catalyst system is also very effective for the cycloaddition of relatively unreactive styrene oxide and CO₂ with a significantly high $6.6 \times 10^3 \text{ h}^{-1}$ TOF. In general, the styrene oxide is a bulky epoxide and its conversion to styrene carbonate is low compared with that of propylene oxide to the corresponding cyclic carbonates, probably due to the low reactivity of the β -carbon atom of styrene oxide. Although a few different catalyst systems have been reported for the coupling of carbon dioxide and styrene oxide [2f,2k,2l,4c,7], they can only

Table 3
Coupling of CO₂ and various epoxides^a

Entry	Substrate	Product	Epoxides/ZnBr ₂ ^b	Yield (%) ^c	TOF (h ⁻¹) ^d
1			7000	95	6627
2			11000	92	10103
3			9000	90	8120
4			3000	65	1958

^a Reaction conditions: hexabutylguanidinium bromide/ZnBr₂ = 6:1, ZnBr₂: 0.00002 mmol; CO₂ initial pressure: 3 MPa; temperature: 130 °C; time: 1 h.

^b The molar ratio of epoxides to ZnBr₂.

^c Isolated yield.

^d Moles of cyclic carbonate produced per mole of catalyst per hour.

offer $\text{TOF} < 3000 \text{ h}^{-1}$ value. Furthermore, we have also found a dramatically high $10 \times 10^4 \text{ h}^{-1}$ TOF for the epichlorohydrin, which may be attributed to the presence of the electron withdrawing chloromethyl group. Besides the terminal epoxides, we also examined the cyclohexene oxide in this transformation under the same reaction conditions, obtaining the corresponding cyclic carbonate in $2.0 \times 10^3 \text{ h}^{-1}$ TOF (entry 4). To our knowledge, these are among the highest TOF values ever reported in the literature. In addition, it is worthy to note that propylene oxide has higher reactivity than other epoxides, but in this present work it gives a lower $8.6 \times 10^3 \text{ h}^{-1}$ TOF value (Table 2, entry 7). The reasons for this occurrence are still not clear at this stage.

3.3. The possibility of recycling of the catalyst system

It is well known that the stability and reusability of a catalyst system are the two key factors that determine whether it finds practical application in industry. In order to test this characteristic of the novel catalyst system, the cycloaddition of propylene oxide and CO_2 was carried out under the optimum conditions. After the reaction, propylene carbonate and unreacted propylene oxide were distilled off from the product mixture, and the remaining catalyst was reused for further reactions directly. As shown in Table 4, through five successive recycles, no significant drop in either the yield or the selectivity is observed.

Table 4

Catalyst recycling studies with guanidinium $\text{E}/\text{ZnBr}_2 = 6:1^{\text{a}}$

Number of recycle	Yield (%) ^b	TOF (h^{-1}) ^c
1	99.5	8560
2	98.3	8450
3	99.0	8510
4	98.7	8485
5	98.1	8435

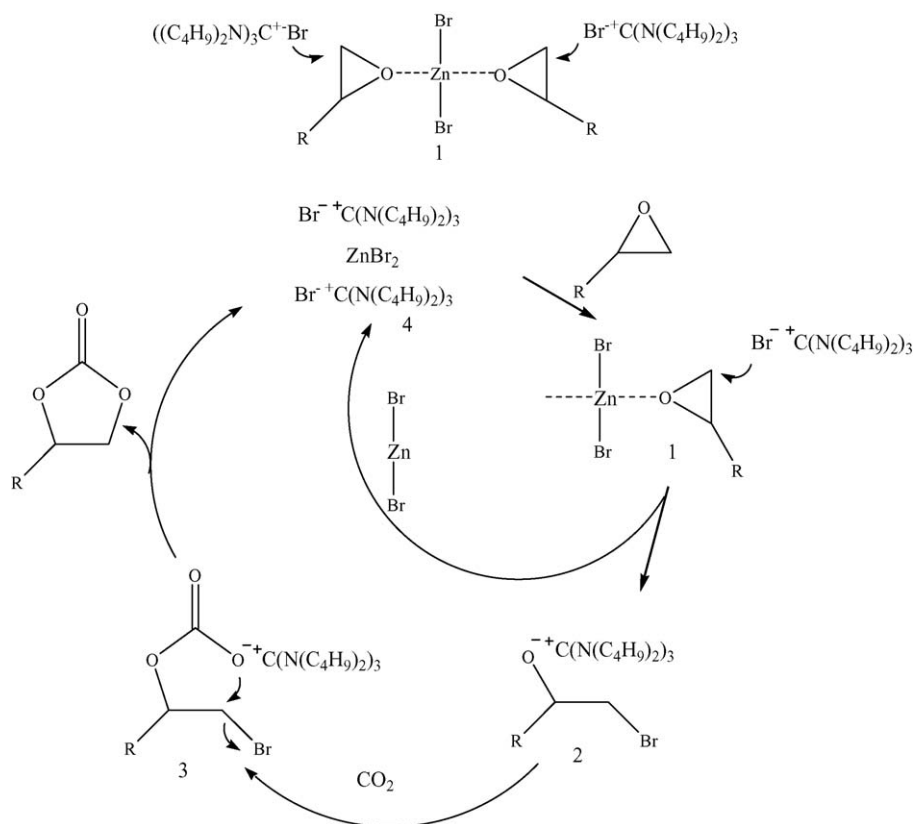
^a Reaction conditions: propylene oxide (PO) (12 ml, 0.172 mol); ZnBr_2 (0.00002 mol); pressure: 3 MPa; time: 1 h; temperature: 130°C .

^b Isolated yield, the selectivity $>99\%$.

^c Moles propylene carbonate produced per mole of catalyst per hour.

4. Mechanistic consideration

As to the catalytic mechanism for this coupling reaction using similar Lewis acid–base catalyst system (bi-functional catalyst system) [7], it is widely recognized that at first the epoxide is coordinated with the Lewis acid site Zn to form the adduct of the metal–epoxide complex, followed by the ring opening of the epoxide by means of a nucleophilic attack by Lewis base, which leads to an oxy anion species affording the corresponding cyclic carbonate after the reaction with CO_2 by intramolecular cyclic elimination. Based on the experimental results obtained, we speculate that this catalyst system also undergoes a similar catalytic process (Scheme 3), and that the higher catalytic activity of this catalyst system than that of quaternary ammo-



Scheme 3.

nium salts, imidazolium salt and pyridinium salt [21,4d,7] could be ascribed to the special steric and electrophilic characteristics of hexabutylguanidinium salt [8,9]. The bulkiness of hexabutylguanidinium ion makes the electrostatic interaction between the cation and the anion weakened, which render counter anions (bromide ion and oxy anion) more nucleophilic. The increased nucleophilicity of anions and high leaving ability of bromide anion incorporated with hexabutylguanidinium cation results in the rate enhancement of the ring opening of epoxide and intramolecular cyclic elimination. Considering that the yield of propylene carbonate increases with increasing molar ratio of guanidinium to zinc bromide, we speculate that $ZnBr_2$ only participates in the ring-opening of epoxides. When the ratio of guanidinium to $ZnBr_2$ is up to 6:1, they attain to a balance, and the best catalytic activity is obtained.

5. Conclusions

We have demonstrated that a novel catalyst system based on hexabutylguanidinium bromide/ $ZnBr_2$ exhibits significant catalytic activity and selectivity for the synthesis of cyclic carbonates from cycloaddition between carbon dioxide and epoxides under mild conditions, without any additional co-solvents. The catalyst system can be reused up to at five times without significant drop in either the yield or the selectivity. Furthermore, it is an air stable, cheap and environmentally benign catalyst system. These characteristics make it an ideal catalyst system in terms of potential industrial application in chemical fixation of carbon dioxide. The special steric and electrophilic characteristics of hexabutylguanidinium bromide ionic liquid result in the prominent performance of this novel catalyst system.

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