

# Chemical Fixation of Carbon Dioxide by Zinc Halide/ $\text{PPh}_3$ / $n$ - $\text{Bu}_4\text{NBr}$

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**Abstract** An efficient catalyst system composed of  $\text{ZnX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{PPh}_3$  (triphenylphosphine) and  $n\text{-Bu}_4\text{NBr}$  (tetrabutylammonium bromide), was developed and showed high activity and selectivity for the coupling reaction of  $\text{CO}_2$  and epoxide under mild conditions. The effects of reaction temperature,  $\text{CO}_2$  pressure, reaction time and various compositions of the catalysts were investigated. It turned out that the yield for the coupling reaction of  $\text{CO}_2$  and propylene oxide (PO) could reach 98.1% in the presence of  $\text{ZnBr}_2/\text{PPh}_3/n\text{-Bu}_4\text{NBr}/\text{PO}$  (molar ratio of 10 : 1 : 2 : 1783) at a low pressure of  $\text{CO}_2$  (3 MPa), short time (5 h) and mild temperature (130 °C) without any organic solvents. The catalyst system was applicable to other six terminal epoxides.

**Keywords** chemical fixation; carbon dioxide; cyclic carbonate; Zinc halide; composite catalyst system

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## 卤化锌/ $\text{PPh}_3$ / $n$ - $\text{Bu}_4\text{NBr}$ 催化体系催化二氧化碳的化学固定

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**摘要** 研究了由卤化锌、三苯基膦、四丁基溴化铵 3 种组分组成的一种高效的催化体系, 在温和条件下, 对催化  $\text{CO}_2$  与环氧烷耦合反应能够得到高的催化活性和选择性. 系统考察了反应温度、 $\text{CO}_2$  压力、反应时间和不同的催化剂组分对催化活性的影响. 结果表明: 催化体系  $\text{ZnBr}_2/\text{PPh}_3/n\text{-Bu}_4\text{NBr}/\text{PO}$  的摩尔比为 10 : 1 : 2 : 1783, 在  $\text{CO}_2$  压力为 3 MPa、反应时间 5 h、反应温度为 130 °C 及无任何有机溶剂的情况下产率可达 98.1%. 此催化体系对其他 6 种环氧烷也有很好的催化效果.

**关键词** 化学固定; 二氧化碳; 环状碳酸酯; 卤化锌; 复合催化体系

Nowadays, with the increase of  $\text{CO}_2$  emissions, the greenhouse effect has become a major problem<sup>[1]</sup>. The fixation of  $\text{CO}_2$  has been a challenge for synthetic chemistry and has recently attracted much interest in view of the green chemistry<sup>[2]</sup>. As one of the effective routes for chemical fixation of  $\text{CO}_2$ , the synthesis of cyclic carbonates by the coupling reactions of epoxides and  $\text{CO}_2$  have been extensively investigated<sup>[3]</sup>. Consequently, various kind of catalysts and catalytic systems have been developed, including phosphonium iodide, transition metal complexes, supported metal complexes, electroreduction, and ionic liquids<sup>[4]</sup>. Hence, it is desirable to develop new types of active and stable catalysts that are highly active for the

coupling reaction of epoxides and  $\text{CO}_2$ , but almost inert to the decomposition reactions of cyclic carbonates.

Herein, we reported an extremely simple, solvent-free, air-insensitive, cheap catalyst with shorter reaction time and high selectivity and ecologically safer route to cyclic carbonate from the reactions of epoxide with  $\text{CO}_2$  in the presence of catalytic amounts of Zinc halide,  $\text{PPh}_3$  and  $n\text{-Bu}_4\text{NBr}$ .

## 1 Experimental

$^1\text{H}$  NMR spectra were recorded on a Bruker Al-400 MHz instrument using trimethylsilane (TMS) as an internal standard. All spectra were recorded at room temperature. All the known compounds were identified

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by comparison of their physical and spectral data with those in previous reports. The epoxides were distilled from  $\text{CaH}_2$ .

General procedure for synthesis of cyclic carbonates: A stainless steel autoclave (250 mL) dried in vacuo containing catalysts was linked to  $\text{CO}_2$  cylinders. A prescribed amount of epoxide was added with a hypodermic syringe. The catalysts were successively charged into the reactor without using any additional solvent. The reactor vessel was placed under a constant pressure of  $\text{CO}_2$  for 20 min to allow the system to equilibrate and then heated to the desired temperature under stirring. After cooling to ambient

temperature, the result mixture was transferred to a 50 mL round bottom flask. The unreacted propylene oxide was removed in vacuo, the product was obtained as a colorless liquid. All the cyclic carbonates were identified by GC/MS (HP6890/5973) and 400 MHz NMR.

## 2 Results and Discussion

During our investigation of the cycloaddition between  $\text{CO}_2$  and PO catalyzed by  $\text{ZnX}_2$  in the presence of quaternary salts and  $\text{PPh}_3$  (Fig. 1) it turned out that the propylene carbonate could be obtained in 98.1 % yield without using any co-solvents (Tab. 1, entry 22).

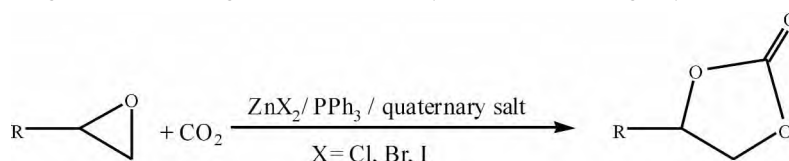


Fig. 1 Synthesis of cyclic carbonates from epoxides and  $\text{CO}_2$

图1 环氧烷与  $\text{CO}_2$  合成环状碳酸酯

表1 不同反应参数对  $\text{CO}_2$  与 PO 耦合反应结果的影响

Tab. 1 Effect of reaction parameters on the coupling of  $\text{CO}_2$  and PO

Entry <sup>[a]</sup>	Catalytic system	$T/^\circ\text{C}$	$P/\text{MPa}$	$t/\text{h}$	Yield/% <sup>[b]</sup>
1	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	93.4
2	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NCl}$	130	3	5	60.8
3	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NI}$	130	3	5	73.8
4	$\text{ZnCl}_2 / \text{PPh}_3 / \text{Et}_4\text{NBr}$	130	3	5	45.9
5	$\text{ZnCl}_2 / \text{PPh}_3 / \text{DMAP}$	130	3	5	33.7
6	$n\text{-Bu}_4\text{NBr}$	130	3	5	30.8
7	$\text{ZnCl}_2$	130	3	5	12.6
8	$\text{ZnCl}_2 / n\text{-Bu}_4\text{NBr}$	130	3	5	74.6
9	$\text{ZnCl}_2 / \text{PPh}_3$	130	3	5	9.5
10	$\text{PPh}_3$	130	3	5	5.6
11	$\text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	21.1
12	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	110	3	5	66.0
13	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	90	3	5	44.2
14	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	70	3	5	14.9
15	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	8	3	5	4.6
16	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	1	9.1
17	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	3	73.8
18	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	7	85.5
19	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	1	5	32.6
20	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	5	5	37.3
21	$\text{ZnCl}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	7	5	33.5
22	$\text{ZnBr}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	98.1
23	$\text{ZnI}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	97.0
24	$\text{ZnEt}_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	54.3
25	$\text{Zn}(\text{CH}_3\text{COO})_2 / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	89.9
26	$\text{Zn} / \text{PPh}_3 / n\text{-Bu}_4\text{NBr}$	130	3	5	79.4

<sup>[a]</sup> Reaction conditions: propylene oxide (15 mL, 12.44 g, 0.214 mol),  $r(\text{ZnBr}_2 : \text{PPh}_3 : n\text{-Bu}_4\text{NBr} : \text{PO}) = 10 : 1 : 2 : 1783$ , the selectivity to products are all more than 99 %; <sup>[b]</sup> Isolated yields

### 2.1 The effect of $\text{CO}_2$ pressure

The effect of  $\text{CO}_2$  pressure on the catalytic activity was studied at  $130\text{ }^\circ\text{C}$  and 5 h under the pressure of 1.0 ~ 7.0 MPa, as can be seen in Fig. 2, the product propylene carbonate (PC) yield increased to 1.0 ~ 3.0 MPa, which probably because PC is in its liquid form under the adopted reaction conditions, the increase of  $\text{CO}_2$  pressure should be a favorable factor for PO conversion<sup>[5]</sup>. However, when the pressure reached to 3.0 ~ 7.0 MPa, the yield decreased immediately (Tabl. 1, entries 1, 19 ~ 21), which could be attributed to the decrease in polarity of  $\text{CO}_2$  with an increase in pressure. The polarity change resulted in the solubility decrease of the catalyst in  $\text{CO}_2$ <sup>[6]</sup>.

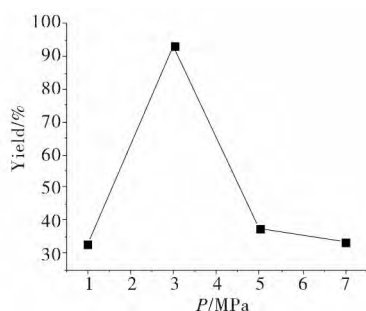


Fig. 2 Effect of  $\text{CO}_2$  pressure on the PC yield

图 2  $\text{CO}_2$  压力对 PC 产率的影响

### 2.2 The effect of reaction time

The effect of reaction time on the catalytic activity was studied at  $130\text{ }^\circ\text{C}$  and 3 MPa in 1 ~ 7 h (Fig. 3). The PC yield increased rapidly within 5 h, but the yield decreased at 7 h. (Tab. 1, entries 1, 16 ~ 18). It can be explained that the contact between the catalytically active site and the reaction substrates became more and more difficult along with the increase of PC amount in the reaction system, which could be attributed to the increasing viscosity<sup>[7]</sup>.

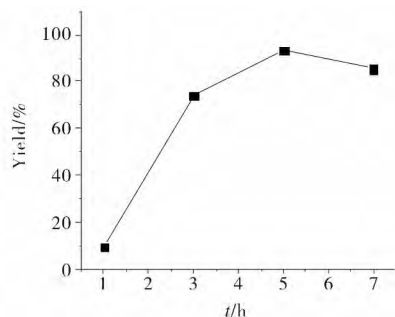


Fig. 3 Effect of reaction time on the PC yield

图 3 反应时间对 PC 产率的影响

### 2.3 The effect of reaction temperature

Reaction temperature is a very important factor for the cycloaddition of  $\text{CO}_2$  with epoxides, different temperature even would lead to different product. Herein, the reaction time effect was studied at 5 h and 3 MPa under  $60\text{ }^\circ\text{C}$  ~  $130\text{ }^\circ\text{C}$  (Tab. 1, entries 1, 12 ~ 15). As can be seen from Fig. 4, the PC yield is nearly proportional to reaction temperature and the reaction almost complete at  $130\text{ }^\circ\text{C}$ , which indicated that the reaction reacted most during this interval<sup>[8]</sup>.

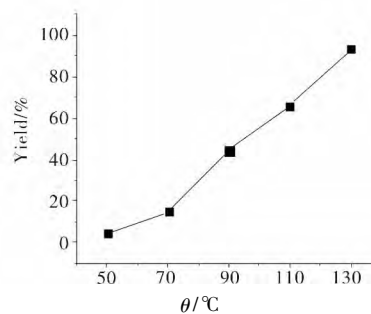


Fig. 4 Effect of reaction temperature on the PC yield

图 4 反应温度对 PC 产率的影响

### 2.4 The effect of various catalytic systems

Basing on the above results, the effect of various catalytic systems for the coupling reaction of PO and  $\text{CO}_2$  were tested at  $130\text{ }^\circ\text{C}$ , 5 h and 3 MPa, the results were also summarized in Tab. 1. It's well known that the Lewis base is the most common used co-catalyst, especially quaternary salts. Four kinds of quaternary salts ( $n\text{-Bu}_4\text{NBr}$ ,  $n\text{-Bu}_4\text{NCl}$ ,  $n\text{-Bu}_4\text{NI}$  and  $\text{Et}_4\text{NBr}$ ) were investigated as the co-catalyst, and it turned out that highest PC yield was obtained with  $n\text{-Bu}_4\text{NBr}$  as co-catalyst under the same conditions (Tab. 1, entries 1 ~ 4). This could be explained considerably that the catalytic activity of the halide is determined by a balance between its nucleophilicity and leaving-group ability. A good nucleophile would favour the initial opening of the epoxide ring, but it would also be a worse leaving group in the last step of the reaction, i. e. in the back-biting reaction leading to the formation of cyclic carbonate<sup>[9]</sup>. 4-Dimethylaminopyridine (DMAP) was also a co-catalyst for the coupling reaction. As an organic base, DMAP could activate  $\text{CO}_2$  to form an organic base- $\text{CO}_2$  intermediate, which was different from quaternary ammonium salt<sup>[10]</sup>. However, DMAP showed much lower catalytic activity

than quaternary ammonium salts ( Tab. 1 , entry 5 ) , which indicated that the reaction mechanism of *n*-Bu<sub>4</sub>NBr was different from the system with DMAP as the co-catalyst.

Since the catalytic system was multi-compounded , it was supposed that a synergistic effect should exist<sup>[11]</sup>. To confirm the proposal , some catalytic systems were also tested without quaternary ammonium salt , ZnCl<sub>2</sub> and PPh<sub>3</sub> severally , and the component ZnCl<sub>2</sub> , *n*-Bu<sub>4</sub>NBr , PPh<sub>3</sub> was solely used as a single catalyst for this reaction as well. The PC yield dropped for all the tested system as expected ( Tab. 1 , entries 1 , 6 ~ 11 ) , which indicated that there's some inhibitory effect between *n*-Bu<sub>4</sub>NBr and PPh<sub>3</sub>.

### 2.5 Proposed mechanism

From the results above , a proposed mechanism was deduced in Fig. 5. The catalytic system has two

catalytic cycles , the quaternary salts open the ring of the epoxide to produce an oxyanion species. That may be why the yield was rather low when the quaternary salt was absent ( Tab. 1 , entry 9 ) . While in the other cycle , it is the ZnX<sub>2</sub>( PPh<sub>3</sub>)<sub>2</sub> formed in situ during the early phase of the coupling reaction performed in the presence of ZnCl<sub>2</sub> and triphenylphosphine ( PPh<sub>3</sub>) which activated the inert CO<sub>2</sub><sup>[12]</sup>. Then the metal centre ZnCl<sub>2</sub> was replaced by ZnBr<sub>2</sub> , ZnI<sub>2</sub> , ZnEt<sub>2</sub> , Zn ( CH<sub>3</sub>COO )<sub>2</sub> , Zn ( Tab. 1 , entries 22 ~ 26 ) . The results showed that the catalytic activity order was ZnBr<sub>2</sub> ≥ ZnI<sub>2</sub> > ZnCl<sub>2</sub> > Zn ( CH<sub>3</sub>COO )<sub>2</sub> > Zn > ZnEt<sub>2</sub> , which suggested that leaving-group ability of the anions seem to play an important role in the process of CO<sub>2</sub> inserting<sup>[13]</sup>.

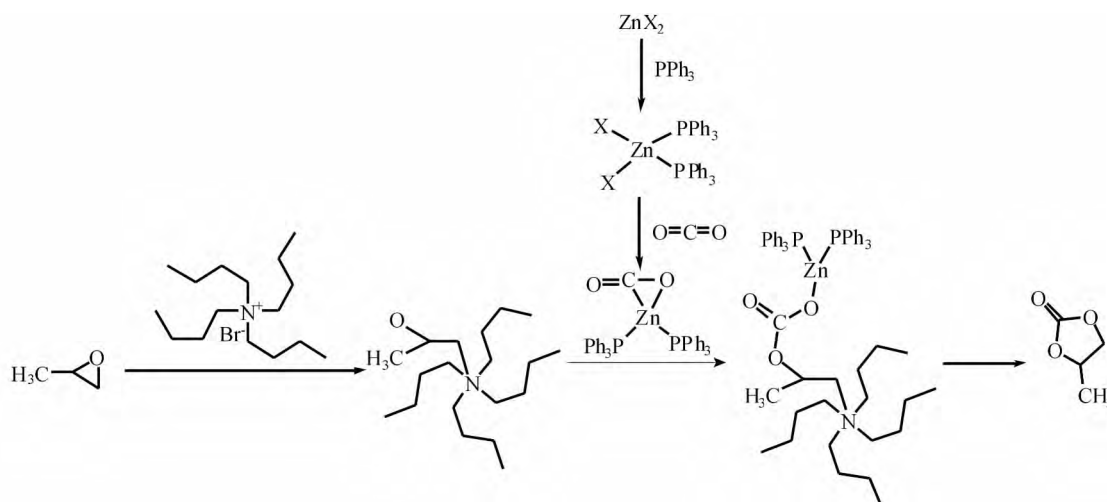


Fig. 5 The plausible mechanism for the cycloaddition of CO<sub>2</sub> with PO catalyzed by ZnX<sub>2</sub> ( X = Cl , Br , I ) , PPh<sub>3</sub> and *n*-Bu<sub>4</sub>NBr


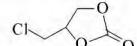
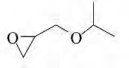
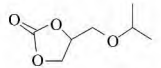
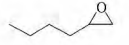
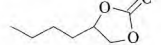

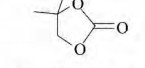
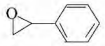
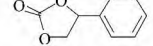

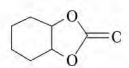
图5 由卤化锌、三苯基膦和四丁基溴化铵催化 CO<sub>2</sub> 与环氧丙烷环加成反应的可能机理

### 2.6 Cycloaddition reaction of various epoxides and CO<sub>2</sub>

To extend the scope of the coupling reaction , six epoxides ( epichlorohydrin , glycidyl isopropyl ether , 1,2-epoxyhexane , isobutylene oxide , styrene oxide , cyclohexene oxide ) were used as substrates and reacted with CO<sub>2</sub> under optimized and solventless reaction conditions ( 130°C , 5 h , 3 MPa ) . The cycloaddition results shown in Tab. 2 indicated that the catalyst system could convert all the general epoxides studied to the corresponding cyclic carbonates

effectively under mild conditions. Among them , epichlorohydrin ( Tab. 3 , entry 1 ) , glycidyl phenyl ether ( Tab. 3 , entry 2 ) , 1,2-epoxyhexane ( Tab. 3 , entry 3 ) and styrene oxide ( Tab. 3 , entry 5 ) gave the relevant cyclic carbonate with more than 90% yield. However , when isobutylene oxide ( Tab. 3 , entry 4 ) and cyclohexene oxide ( Tab. 3 , entry 6 ) were used as substrate , the yields were dramatically lower than others. This might be due to the low reactivity of electron-rich substrates and bigger steric hindrance<sup>[14]</sup>.

Tab. 2 The coupling results of various epoxides and  $\text{CO}_2$ 表 2 其他环氧烷与  $\text{CO}_2$  耦合反应结果

Entry <sup>[a]</sup>	Substrate	Product	Yield[%] <sup>[b]</sup>
1			96.0
2			99.1
3			96.4
4			18.4
5			96.0
6			26.1

<sup>[a]</sup> Reaction conditions: epoxides (0.214 mol),  $r(\text{ZnBr}_2 : \text{PPh}_3 : n\text{-Bu}_4\text{NBr} : \text{PO}) = 10 : 1 : 2 : 1783$ ,  $P = 3 \text{ MPa}$ ,  $T = 130 \text{ }^\circ\text{C}$ ,  $t = 5 \text{ h}$ , the selectivity to products are all more than 99 %;

<sup>[b]</sup> Isolated yields.

### 3 Conclusion

The efficient catalytic system composed of  $\text{ZnX}_2/\text{PPh}_3/n\text{-Bu}_4\text{NBr}$  was developed for the coupling reaction between epoxide and  $\text{CO}_2$ . It was found that high conversion, more than 99.0% selectivity, and high PC yield (more than 90%) could be achieved in the presence of  $\text{ZnX}_2/\text{PPh}_3/n\text{-Bu}_4\text{NBr}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) for the synthesis of cyclic carbonates under the mild conditions ( $130 \text{ }^\circ\text{C}$ ,  $3 \text{ MPa}$ ,  $5 \text{ h}$ ) without any organic solvents. The catalytic system was also tested for their activity with various other epoxides and was found to yield considerable amount of corresponding cyclic carbonates under similar conditions. In addition, the mechanism for the coupling reaction was also discussed which could explain the reaction results satisfactorily.

### Acknowledgements

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