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Histidine-catalyzed synthesis of cyclic carbonates in supercritical carbon dioxide

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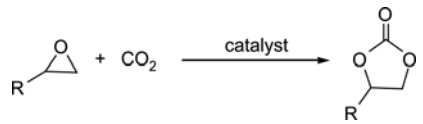
The coupling reaction of carbon dioxide with epoxides was investigated using naturally occurring α-amino acids as the catalyst in supercritical carbon dioxide and it was found that L-histidine is the most active catalyst. In the presence of 0.8 mol% of L-histidine at 130 °C under 8 MPa of CO_2, the reaction of carbon dioxide with epoxides proceeded smoothly, affording corresponding cyclic carbonates in good to excellent yields.

supercritical carbon dioxide, amino acids, epoxides, cyclic carbonates

1 Introduction

Due to oil depletion, mankind is faced with the challenge of finding new carbon resources to get rid of oil dependence. The combustion of fossil fuels produced large amounts of carbon dioxide, which is the primary source of the green house effect. Thus it is very significant to develop efficient processes of capture, fixation and transformation of carbon dioxide. Carbon dioxide can be employed as an abundant and inexpensive C 1 feedstock. Recently, transformation of carbon dioxide into valuable chemicals has drawn much attention from governments, academic fields as well as industry fields [1–4]. The synthesis of cyclic carbonates by the coupling reaction of CO_2 and epoxides is one of the most promising and practical methods for the utilization of CO_2 among many examples (Scheme 1). Cyclic carbonates are valuable compounds due to their enlarged application as aprotic polar solvents, electrolytes in secondary batteries, and as valuable intermediates for polymer synthesis [5–7].

Compared with conventional methods using phosgene as the starting material, the synthesis of cyclic carbonates from epoxides and CO_2 is eco-friendly and atom economic. Thus, since Lichtenwalter and Cooper [8] first reported the synthesis of cyclic carbonate from the reaction of carbon dioxide and epoxides in 1956, many researchers have carried out the research in this area. Numerous homogeneous catalysts have been reported, including metal complexes [9–17], ionic liquids [18–21], and alkali metal salts [22, 23]. Heterogeneous catalysts, such as metal oxides [24, 25], silica gel or polystyrene supported salen metal complex [26–28], supported phosphonium or ammonium salt [29–31], ion exchange resins [32], and ion exchange resins supported gold nanoparticles [33], have also been developed.



Scheme 1 Synthesis of carbonate from epoxide and carbon dioxide.

Recently, we have demonstrated that in dichloromethane most of the naturally occurring α-amino acids could effectively catalyze the coupling of CO_2 with epoxides to yield the corresponding cyclic carbonates in excellent yield with high selectivity [34]. In the drive towards the development

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of more environmentally friendly route to the synthesis of cyclic carbonates, herein we investigated the reaction of CO_2 and epoxides in supercritical carbon dioxide using amino acids as catalysts and found that L-histidine is the most efficient catalyst for the reaction among all the amino acids surveyed under supercritical conditions.

2 Experimental

2.1 General experimental section

IR spectra were obtained with a Tensor-27 FTIR spectrometer. GC data were obtained by a GC7900 instrument equipped with an FFAP column (30 m × 0.250 mm × 0.25 μm). ^{1}H NMR spectra were taken on a 400 MHz Bruker DRX-400 spectrometer with tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. MS data were recorded on a Frinnigan Trace DSQ GC-MS spectrometer. Carbon dioxide with a purity of 99.9%, epoxides and amino acids were commercially available and used as received.

2.2 Synthesis of cyclic carbonates

The typical experimental procedure is as follows: propylene oxide (20 mmol) and L-histidine (0.8 mol%) were added into a 15 mL stainless autoclave with a magnetic stirrer, and CO_2 was charged into the reactor to reach the desired pressure. The reactor was then heated to 130 °C for desired reaction time and the pressure was kept constant during the reaction. After the reaction, the reactor was cooled to 0 °C, and extra CO_2 was vented slowly. The crude product was purified by distillation. The cyclic carbonate was identified by IR, GC/MS and 400 MHz ^{1}H NMR. 4-Methyl-1,3-dioxolan-2-one (**2a**): ^{1}H NMR (400Hz, TMS, $CDCl_3$), δ 1.48 (d, J = 3.6 Hz, 3 H, CH_3), 4.01 (t, J = 8 .4 Hz, 1 H, CH), 4.53 (t, J = 8.0 Hz, 1 H, CH), 4.81–4.86 (m, 1 H, CH); IR (film) v: 2898, 2931, 1795, 1481, 1391, 1180, 1120, 1054, cm^{-1}; MS (70 eV) m/z (%): 102[M$^+$], 87, 58, 57, 43 , 29.

3 Results and discussion

3.1 Catalytic activity of different α-amino acids

Twenty common α-amino acids were screened in the coupling reaction of CO_2 with propylene oxide forming propylene carbonate and the results are shown in Table 1. We were delighted to find that L-histidine is the most efficient catalyst for this reaction among all the amino acids surveyed under supercritical conditions. Propylene oxide could be quantitatively transformed into propylene carbonate at 130 °C under 8 MPa of CO_2 in the presence of 0.8 mol% of histidine (Table 1, entry 19). However, other α-amino acids showed lower catalytic activity (Entries 1–18, 20), which is different from the results obtained in dichloromethane. This may be due to the difference in polarity and solubility between supercritical carbon dioxide and dichloromethane.

Table 1 Coupling of propylene oxide with CO_2 catalyzed by various α-amino acids [a)]

Entry	Amino acids	Yield (%)
1	glycine	20
2	L-alanine	19
3	L-leucine	63
4	L-isoleucine	62
5	L-valine	40
6	L-proline	51
7	L-phenylalanine	67
8	L-tryptophan	27
9	L-methionine	45
10	L-asparagine	7
11	L-glutamine	5
12	L-cysteine	10
13	L-serine	14
14	L-threonine	36
15	L-tyrosine	44
16	L-aspartic acid	18
17	L-glutamic acid	15
18	L-arginine	44
19	L-histidine	100
20	L-lysine	78

a) Reaction conditions: propylene oxide (20 mmol), amino acids (0.8 mol%), CO_2 pressure (8 MPa), 130 °C, 48 h.

3.2 Effect of CO_2 pressure

Figure 1 shows the pressure dependence of the yield of propylene carbonate in the presence of L-histidine at 130 °C.

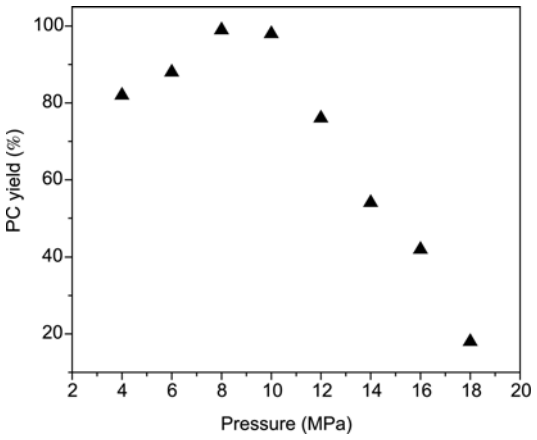


Figure 1 The effect of CO_2 pressure on the yield of propylene carbonate (PC). Reaction conditions: propylene oxide 20 mmol, L-histidine 0.8 mol%, 130 °C, 48 h.

The yield increased with an increase in pressure up to 8 MPa and then dropped sharply at pressures above 12 MPa. A similar correlation between the yield of styrene carbonate and CO_2 pressure was also found in DMF-scCO_2 catalytic system reported previously by Kawanami and coworkers [35]. The main reason may be that at 8 MPa of CO_2 pressure L-histidine dissolved well into the system and led to a high yield of propylene carbonate. While too high CO_2 pressure may cause a low concentration of propylene oxide in the vicinity of the catalyst and resulted in a decrease of the yield.

3.3 Effect of reaction time

The effect of reaction time on the yield is shown in Figure 2. The reaction was carried out in the presence of 0.8 mol% of L-histidine at 130 °C under 8 MPa. The results indicated that the reaction proceeded slowly within the first 18 h and then became fast. However, the rate of the reaction slowed down again after 24 h. A reaction time of 48 h was necessary for the complete conversion of propylene oxide to propylene carbonate.

3.4 Effect of reaction temperature

The influence of reaction temperature on the yield is shown in Figure 3. The catalytic activity of L-histidine was quite sensitive to the reaction temperature and was low at lower temperatures. 15% yield of propylene carbonate was obtained at 90 °C. With the increase of reaction temperature the yield increased. L-histidine showed high catalytic activity at 130 °C and gave 100% yield of propylene carbonate.

3.5 Effect of the dosage of catalysts

To optimize the dosage of catalysts, different amounts of histidine were tested (Figure 4). The reaction could not occur in the absence of any catalyst. Increasing the load of the catalyst the yield of propylene carbonate increased and reached 100% in the presence of 0.8 mol% of L-histidine.

3.6 Synthesis of various cyclic carbonates

Under the optimized reaction conditions, a variety of epoxides were examined for the synthesis of different cyclic carbonates in the presence of L-histidine. As shown in Table 2, all of the mono-substituted terminal epoxides (**1a–1g**) could be transformed into the corresponding five-membered cyclic carbonates in good to excellent yields (Table 2, entries 1–7). Cyclohexene oxide (**1h**) could also react with CO_2 to yield the corresponding carbonate **2h** in 44% yield (Table 2, entry 8), and the lower yield could be attributed to the effect of high steric hindrance of cyclohexene epoxide. According to the ^{1}H, ^{13}C and NOESY NMR spectra of **2h**, we found that the cyclic carbonate produced from cyclohexene oxide was of *cis* stereochemistry.

In addition, although L-histidine is a chiral catalyst, no asymmetric induction was observed. It may be because the reaction requires high temperatures (>90 °C).

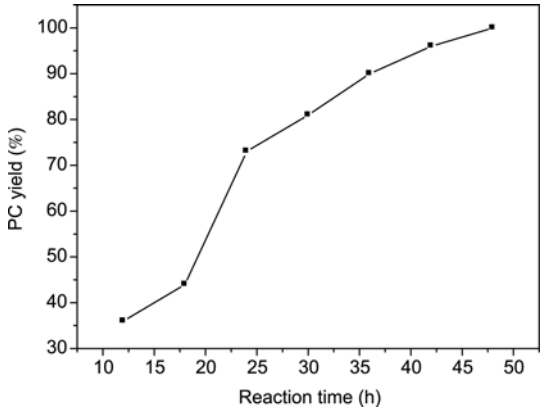


Figure 2 The effect of reaction time on the yield of propylene carbonate (PC). Reaction conditions: propylene oxide 20 mmol, L-histidine 0.8 mol%, 130 °C, 8 MPa.

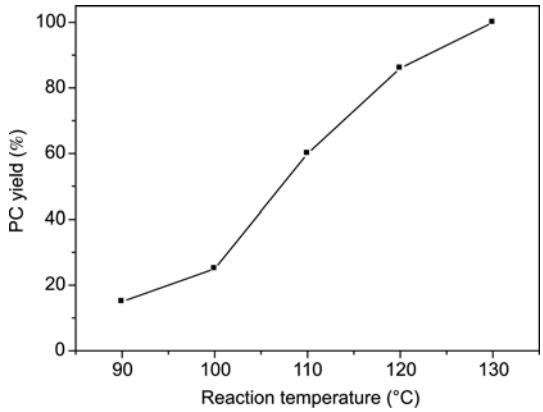


Figure 3 The effect of reaction temperature on the yield of propylene carbonate (PC). Reaction conditions: propylene oxide 20 mmol, L-histidine 0.8 mol%, 8 MPa, 48 h.

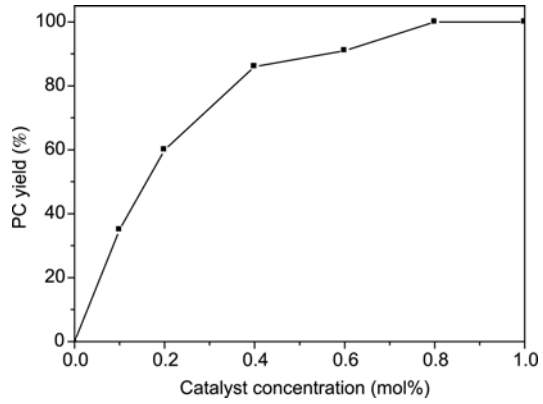
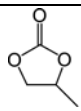
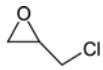
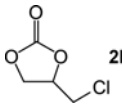
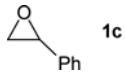
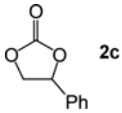
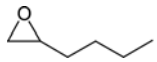
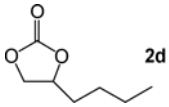
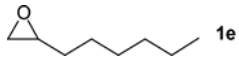
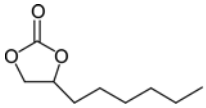
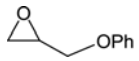
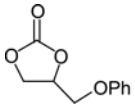
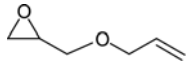
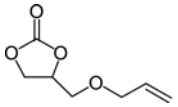
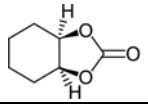


Figure 4 The effect of the dosage of catalysts on the yield of propylene carbonate (PC). Reaction conditions: propylene oxide 20 mmol, 130 °C, 8 MPa, 48 h.

Table 2 Synthesis of various cyclic carbonates in the presence of L-histidine in supercritical carbon dioxide [a)]

Entry	Epoxide	Product	Selectivity (%) [b)]	Yield (%) [c)]
1	 1a	 2a	100	100
2	 1b	 2b	99	95
3	 1c	 2c	99	86
4	 1d	 2d	99	75
5	 1e	 2e	98	77
6	 1f	 2f	100	100
7	 1g	 2g	100	92
8	 1h	 2h	99	44

a) Reaction conditions: epoxide 20 mmol, histidine 0.8 mol%, pressure 8 MPa, 130 °C, 48 h; b) determined by GC; c) isolated yield.

4 Conclusions

In summary, we demonstrated that among the twenty common α-amino acids investigated, L-histidine is the most active catalyst for the coupling reaction of CO_2 with epoxides under supercritical conditions. The reaction temperature, reaction time, CO_2 pressure and the dosage of catalysts have great influence on the reaction. In the presence of 0.8 mol% of L-histidine at 130 °C under 8 MPa of CO_2, the reaction of carbon dioxide with epoxides proceeded smoothly, affording the corresponding cyclic carbonates in good to excellent yields.

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