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Amino Acids/Superbases as Eco-Friendly Catalyst System for the Synthesis of Cyclic Carbonates under Metal-Free and Halide-Free Conditions

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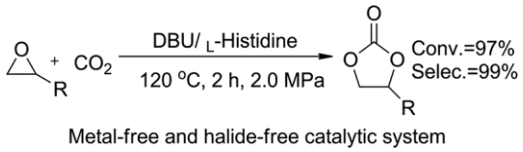
Abstract

An eco-friendly and efficient binary catalyst system of superbases and amino acids was developed for the synthesis of cyclic carbonates from epoxides and CO_2 under metal-free and halide-free conditions. Among the various amino acids and superbases systems tested, the L-histidine/DBU system achieved the highest conversion of propylene oxide and selectivity of propylene carbonate. The effect of various reaction parameters were evaluated. A possible catalyst mechanism for L-histidine synergized with DBU in the ring opening of epoxide and DBU introduced CO_2 activation. The process herein represents a green, simple and cost-effective route for the chemical fixation of CO_2 into cyclic carbonates.

Graphical Abstract



INTRODUCTION

As an attractive C1 feedstock, carbon dioxide (CO_2) is renewable, abundant, inexpensive, nontoxic and nonflammable, so the fixation of CO_2 into useful chemical products has attracted much attention in recent year.[1a, b] Insertion of CO_2 into epoxides to synthesize cyclic carbonates is one of the effectual means of CO_2 fixation.[2a, b, c] The cyclic carbonates could be widely used in many kinds of materials, such as raw materials for synthesizing polycarbonates, electrolytes for batteries, fuel additives and aprotic solvents.[3a, b, c]

A variety of catalysts have been used for this coupling reaction, including metal oxides,[4a, b] metal salen complexes,[5] alkali metal halides,[6] N-heterocyclic carbonates,[4a, 6] ionic liquids,[7a, b] functional organic polymers,[8a, b] porphyrin,[9] organic bases,[10] etc. Most of the catalysts above contain metal cations or halide anions, which have toxicity, certain corrosion resistance and environmentally hazardous problems. It is necessary to explore a metal-free and halide-free catalyst system for this cycloaddition under relative mild conditions.

In recent years, superbases have attracted much attention because they can realize CO_2 capture and activation.[10] They provide excellent CO_2 absorption and chemical activation with high CO_2 capacity and low desorption energy. They can be used to catalyze the cycloaddition reaction of epoxides and CO_2. In recent reports, saccharide,[10c] cellulose[11] and metal compounds[10g, 12] were added to the superbases catalytic system to improve the catalytic efficiency. However, the catalyst systems used were still undesirable in either catalytic activity or environmental protection. Thus, exploration of good catalytic activity and nontoxic superbases catalyst system for the cycloaddition of CO_2 with epoxides into cyclic carbonates is still needed. Amino acids (AA) are natural, abundant, non-toxic biological chemical substances, they are widely used in functional material, catalysts, synthesis of peptide intermediates and chiral solvents.[13a, b] As a natural hydrogen bond donors, amino acids have amino group (e.g. -NH_2, -NH) and strong hydrogen bonding function groups (e.g. -COOH or -OH), He et al.[14] reported that amino acid could activate the epoxide through hydrogen bonding.

In this work, we use the system of amino acids and superbases to catalyze the cycloadditon of epoxides and CO_2. Based on the ability of superbases for CO_2 absorption and activation and the strong hydrogen bonding in amino acids, the system of amino acids and superbases may have better catalytic activity than other metal-free and halide-free catalytic systems

which were mentioned above. In order to test this thought, We have investigated different combination of eight kinds of amino acids and twelve species of organic bases and optimized reaction parameters of cycloaddition. L-Histidine/DBU system achieved the best catalytic activity at 120 ^{o}C, 2 MPa (CO_2 pressure), 2 h.

RESULTS AND DISCUSSION

A variety of amino acids and organic bases were selected to explore the catalytic activity for cycloaddition of epoxides and CO_2 to cyclic carbonates. The amino acids were glycine, L-threonine, L-proline, L-tyrosine, L-histidine, L-lysine, L-aspartic acid and L-trytoplan. The bases were 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), monoethanolamine (MEOA), diethanolamine (DEOA), triethanolamine (TEOA), triethylamine (TEA), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) diethylamine (DEA), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,5,7-tri-azabicyclo[4.4.0]dec-5-ene (TBD), N,N-dimethylaminopyridine (DMAP), pyridine (Py), and tetramethylethylenediamine (TMEDA).

First of all, The amino acids were tested combining with DBU to study the catalytic property of different amino acids by the synthesis of propylene carbonate (PC) from propylene oxide (PO) and CO_2. All the reactions were proceeded at 120 ^{o}C, 2 MPa for 2 h

under solvent free conditions. As is shown in the Table 1, DBU reveals a PO conversion of 86% under 2 MPa of CO_2 pressure (entry 1). The high catalytic activity of DBU might own to its CO_2 activation ability and nucleophilic capability. Amino acids resulted in a PO conversion lower than 20% when it used alone under the employed reaction conditions. In comparison, the system of amino acids and DBU achieved higher catalytic activity than DBU or amino acids, so it indicated that the synergistic action of amino acids and DBU accelerate the reaction rate. In the presence of DBU, the activity order for the amino acids is $_L$-histidine ($_L$-his) > $_L$-threonine ($_L$-thr), $_L$-aspartic acid ($_L$-asp), $_L$-tryptophan ($_L$-try) > glycine (gly) > $_L$-proline ($_L$-pro), $_L$-tyrosine ($_L$-tyr) > $_L$-lysine ($_L$-lys). $_L$-Histidine combined with DBU achieved the highest PO conversion of 97% with selectivity for PC in excess of 99% under the same condition. Therefore, $_L$-histidine was used for the further research.

In order to know the reasons why the addition of amino acids achieved better catalytic activity, we explored the interaction of $_L$-histidine and epoxides, which were confirmed by IR (Scheme 3). Because of the high volatility of PO, We explore the interaction of $_L$-histidine with other epoxides. The characteristic absorbance of NH_3^+ region of the zwitterionic $_L$-histidine is 3015.2 cm^{-1} without epoxides. However, the interaction between NH_3^+ region of the zwitterionic $_L$-histidine and 2,2-dimethyloxirane leads to a shift of NH_3^+ region from 3015.2 cm^{-1} to 3016.9 cm^{-1} (Scheme 3A). Moreover, the interaction between NH_3^+ region of the zwitterionic $_L$-histidine with styrene oxide and 1,2-epoxyheane were

also investigated (Scheme 3B and Scheme 3C). The signal absorbance of NH_3^+ region of the zwitterionic L-histidine shifts downfield from 3015.2 cm^{-1} to 3031.2 cm^{-1} in Scheme 3B. The absorbance of NH_3^+ region of the zwitterionic L-histidine shifts downfield from 3015.2 cm^{-1} to 3017.4 cm^{-1} in Scheme 3C. Those also suggest stronger interaction between epoxides and the NH_3^+ region of the zwitterionic L-histidine.

Different organic bases were examined on the cycloadditon reaction of PO and CO_2 in the presence of L-histidine, the corresponding results were shown in Table 2. From Table 2, we can find that the organic bases exhibited different performance, DBU achieved higher catalytic activity than others. When the DBU was replaced by Py, an unsatisfactory result was obtained with only a 76% PO conversion.

According to the report, the organic base which has a lower pK_a value would lead to a less negative Gibbs free energy of the reaction of CO_2.[15] Hence, the activation ability of the superbases to CO_2 bases on the established pK_a might increase in the order of TEOA < DABCO < DEOA < TMEDA < MEOA < DEA < Py < DMAP < TEA < DBU < MTBD < TBD. While, Table 2 indicates that the actually activity order of the superbases has no direct effect with the pK_a, the increasing order is Py < MEOA < TEA < DEA < TBD < TEDMA < MTBD < DEOA, TEOA < DABCO < DMAP < DBU. The possible reason for this phenomenon is that the synergistic effect of hydroxyl groups in L-histidine and the

steric hindrance of superbases make a bigger difference in the catalytic activity. According to the discussions above, L-histidine/DBU catalyst system was selected for the further survey research. .

Subsequently, the influence of reaction conditions on the fixation of CO_2 to PO was studied. Table 3 shows the effect of the molar ratio of DBU to L-histidine by regularly changing the amount of DBU at a fixed weight of L-histidine (2% molar ratio to PO). It can be seen that the catalyst activity increased apparently with the increasing molar ratio of DBU to L-histidine from 1:2 to 5:1. However, it did not bring about any increase when the molar ratio is higher than 5:1. It is because the concentration of catalyst is high enough to catalyze the reaction. According to the result discussed above, L-histidine/DBU catalytic system shows highest catalytic activity at a molar ratio of 5:1 (DBU to L-histidine).

Subsequently, we investigated the effects of other parameters on the catalytic activity of L-histidine/DBU. Figure 1 shows that the temperature also has a great influence on the PO conversion and PC selectivity in the range of 80-140 ^{o}C. A low conversion of PO was obtained at 80 ^{o}C, the catalytic activity increased sharply from 80 ^{o}C to 110 ^{o}C, the conversion of PO reached highest at 120 ^{o}C with 97% PO conversion and PC selectivity more than 99%. When the reaction temperature was higher than 120 ^{o}C, the conversion of

PO kept stable and selectivity of PC decreased. It may be because the high temperature promotes the formation of by-products. 120 ^{o}C could be the optimal temperature, which was used for further survey research.

Next, the dependence of PO conversion and PC selectivity on the reaction pressure was also evaluated (Figure 2). The CO_2 pressure also has a large influence on the PO conversion at 120 ^{o}C with the increasing pressure between 1.0 MPa to 3.0 MPa. Variation of CO_2 pressure from 1.0 MPa to 2.0 MPa induced a sustaining increased from 88% to 97%. However, with the increasing of CO_2 pressure beyond 2.0 MPa, the PO conversion keeps almost unchanged, the selectivity of PC decreased. The reason for this phenomenon may be that the increasing concentration of CO_2 lead to lower PO concentration around catalyst.[16]

The reaction time was also found to play an important role in the $_{L}$-histidine/DBU-catalyzed cycloaddtion reaction of epoxides and CO_2, which was demonstrated in Figure 3. The conversion of PO achieved 85% in 0.5 h and it approached to 97% in 2 h, thereafter, the conversion of PO kept stable after 2 h. The reason for this phenomenon may be that the reaction has reached a stable state.

In order to evaluate the binary catalyst system of different epoxides, various epoxides were explored in the present of DBU and L-histidine. The results were summarized in Table 4. It can be found that the catalyst system is available to the monosubstituted and disubstituted epoxides. Among the monosubstituted terminal epoxides (1a-1f), the conversion of epoxides were decreased gradually in the order of epoxides ethylene oxide (1a) > propylene oxide (1b) > butyloxirane (1d) > epichlorohydrin (1c) > cyclohexene oxide (1e). Disubstituted epoxides showed (1f, 1h) lower activity than mono-substituted epoxides (1a-1e). Compared to other epoxides, 1,2-epoxyethylbenzene (16h) needed a much longer reaction time to get a high conversion (98%).

Possible Mechanism For The Cycloaddtion Of Epoxide With CO_2

According to the previous reports and experiment results obtained,[16] the possible mechanism for the cycloadditon of CO_2 and epoxide by L-histidine/DBU system was proposed in Scheme 5. In step 1, the oxygen of epoxide ring was activated by the NH_3^+ region of zwitterionic L-histidine, at the same time, the DBU made a nucleophilic attack on the less sterically hindered carbon atom of the epoxide ring, then the ring-opened immediate 1 would be formed. In parallel, another DBU might interact with the eletrophilic carbon atom of the CO_2 molecule to provide a carbon Salt 2. Subsequently, the immediate 1 made the nucleophilic attack on the carbon Salt 2, a new alkyl carbonate Compound 3

would be formed. In the final step, the cyclic carbonate was acquired and the catalyst is regenerated by intramolecular ring closure. In this reaction, L-histidine and DBU had a synergistic influence on the ring opening of epoxide. Meanwhile, DBU had a significant effect on the fixation of CO_2. Therefore, this catalyst system of L-histidine and DBU played a synergetic catalysis role in making the reaction proceed smoothly.

CONCLUSIONS

In summary, an efficient binary catalyst system of superbases and amino acids was developed for the synthesis of cyclic carbonates from epoxides and CO_2 under metal-free and halide-free conditions. Among the various amino acids and superbases, the L-histidine/DBU system had the highest activity and exhibit the maximum 97% PO conversion and 99% PC selectivity. The binary catalyst system was found to apply to other epoxides. A possible catalyst mechanism for L-histidine synergized with DBU in the ring opening of epoxide and the activation of CO_2 induced by DBU was proposed. The catalyst system of L-histidine and DBU played a synergetic catalysis role in making the reaction proceed smoothly. The result of this work furnished an instance of the application of biomaterials combine with superbases as potential material in organic synthesis and catalysis.

EXPERIMENTAL

Synthesis of PC from PO and CO_2 using the DBU/L-histidine catalyst system was performed in a 25 mL pressure reactor equipped with a magnetic stirrer, electrical heating mantle and automatic temperature control system. For each typical batch operation, PO (1 mL, ~14 mmol) and DBU (10% mol) $_L$-histidine (2% mol) were charged into the reactor. Subsequently, CO_2 was charged into the reactor, the pressure was adjusted to 2.0 MPa at 120 ^oC. The reactor was maintained for 2 h, and the pressure and temperature were kept constant during the reaction. After the reaction time closed, cycloaddition was stopped by cooling the reaction mixture to ambient temperature, and the excess CO_2 was vented.

The products were identified by 6280 GC and 6890-5973B GC-MS. ^1H NMR was carried out at room temperature on a Bruker400MHz NMR spectrometer using $CDCl_3$ as solvent. ESI-MS analysis were performed on a Bruker time of flight mass spectrometer micro TOF-Q II using an electrospray ionization (ESI) souce. NMR data and HRMS date of the 4-methyl-1, 3-dioxolan-2-one (**2b**) was provided as follows: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm):1.42-1.43 (d, J=6.0 Hz, 3H), 3.98 (t, J=8.8 Hz, 1H), 4.51 (t, J=8.0 Hz, 1H), 4.79-4.86 (m, 1H); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ (ppm): 19.15, 70.53, 73.48, 154.95 (C=O). HRMS (ESI): m/z calcd for $C_4H_6O_3Na$ $[M+Na]^+$ 125.0784, found 125.0271.

SUPPORTING INFORMATION

Supporting Information: Full experimental detail, ^{1}H and ^{13}C NMR spectra and HRMS date of cyclic carbonates, IR spectra of amino acids with and without PO. This material can be found via the "Supporting Information" section of this article's webpage.

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Table 1. Coupling of PO with CO_2 by different catalysts. [a]

Entry	Base	AA	Results[b]	
			PO conversion/%	PC selectivity/%
1	DBU	/	86	99
2	/	$_L$-His	18	85
3	/	$_L$-Thr	4	81
4	/	$_L$-Asp	Trace	Trace
5	DBU	$_L$-Thr	96	99
6	DBU	Gly	95	99
7	DBU	$_L$-Pro	94	99
8	DBU	$_L$-Tyr	94	99
9	DBU	$_L$-His	97	99
10	DBU	$_L$-Lys	86	99
11	DBU	$_L$-Asp	96	99
12	DBU	$_L$-Trp	96	99

[a] Reaction conditions: PO (1 mL), DBU (10% mol), Amino Acid (2% mol), CO_2 pressure (2.0 MPa), 2 h, 120 ^oC.

[b] Determined by GC through using area normalization method.

Table 2. The effect of bases on the PO conversion and PC selectivity. [a]

Entry	Catalyst	Results[b]	
		PO conversion/%	PC selectivity/%
1	TBD/$_L$-His	90	99
2	MTBD/$_L$-His	93	99
3	DBU/$_L$-His	97	99
4	TEA/$_L$-His	85	99
5	DMAP/$_L$-His	96	95
6	Py/$_L$-His	76	97
7	DEA/$_L$-His	89	99
8	MEOA/$_L$-His	81	99
9	TMEDA/$_L$-His	91	99
10	DEOA/$_L$-His	93	99
11	DABCO/$_L$-His	95	99
12	TEOA/$_L$-His	93	99

[a] Reaction conditions: PO (1 mL), base (10% mol), $_L$-histidine (2% mol), CO_2 pressure (2.0 MPa), 2 h, 120 ^oC.

[b] Determined by GC through using area normalization method.

Table 3. Effect of DBU amount on fixation of CO_2 with PO into PC. [a]

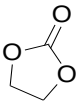
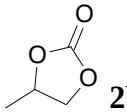
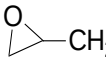
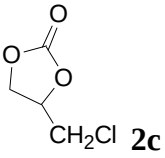
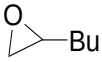
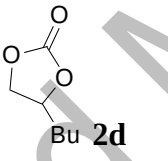
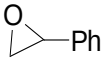
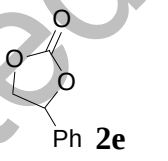
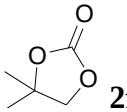
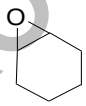
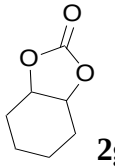
Entry	DBU/$_L$-His	Results[b]	
		PO conversion/%	PC selectivity/%
1	1:2	78	99
2	1:1	90	99
3	3:1	96	99
4	5:1	97	99
5	7:1	97	99

[a] Reaction conditions: PO (1 mL), $_L$-histidine (2% mol), CO_2 pressure (2.0 MPa), 120 ^oC, 2 h

[b]Determined by GC through using area normalization method.

Table 4. Cycloaddition of CO_2 and various epoxides with $_L$-histidine/DBU catalyst system.

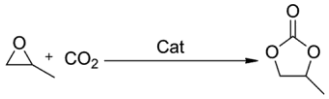
a

Entry	Epoxide	Product	Results[b]	
			Conversion/%	Selectivity/%
1[c]	 **1a**	 **2a**	99[c]	99
2	 **1b**	 **2b**	97	99
3	 **1c**	 **2c**	88	99
4	 **1d**	 **2d**	93	99
5	 **1e**	 **2e**	85	99
6	 **1f**	 **2f**	87	99
7[d]	 **1g**	 **2g**	98[d]	99

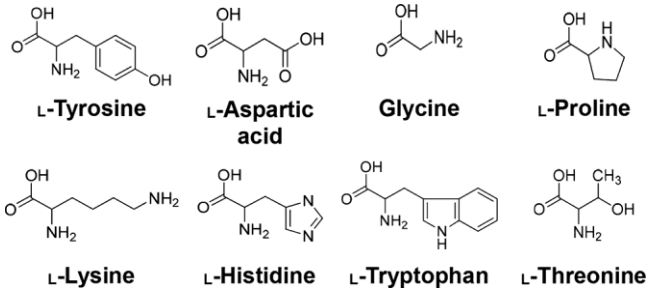
[a] Reaction conditions: epoxide (1 mL), DBU (10% mol), $_L$-histidine (2% mol), CO_2 pressure (2.0 MPa), 2 h, 120 ^oC.

[b] Determined by GC through using area normalization method. [c] 1 h. [d] 16 h.

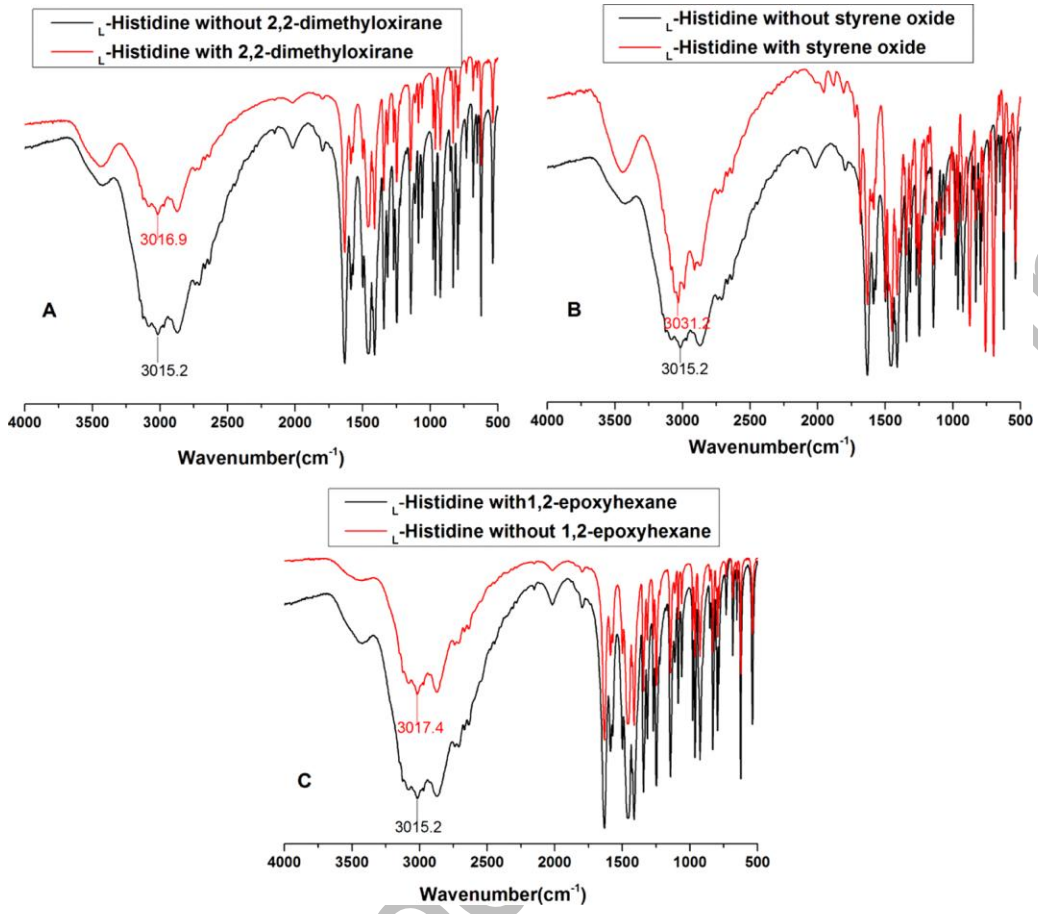
Scheme 1. Cycloadditon of PO and CO_2 using $_L$-histidine/DBU



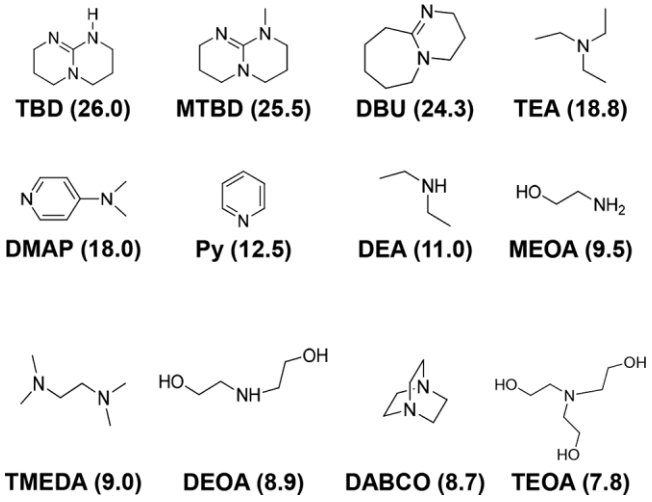
Scheme 2. Chemical structure of amino acids used in this work and their designations.



Scheme 3. The IR spectrum of $_L$-histidine with and without epoxides.



Scheme 4. Chemical structures of organic bases used in this work. The data in parentheses is pK_a value.



Scheme 5. The proposed mechanism for the L-histidine/DBU catalyzed reaction.

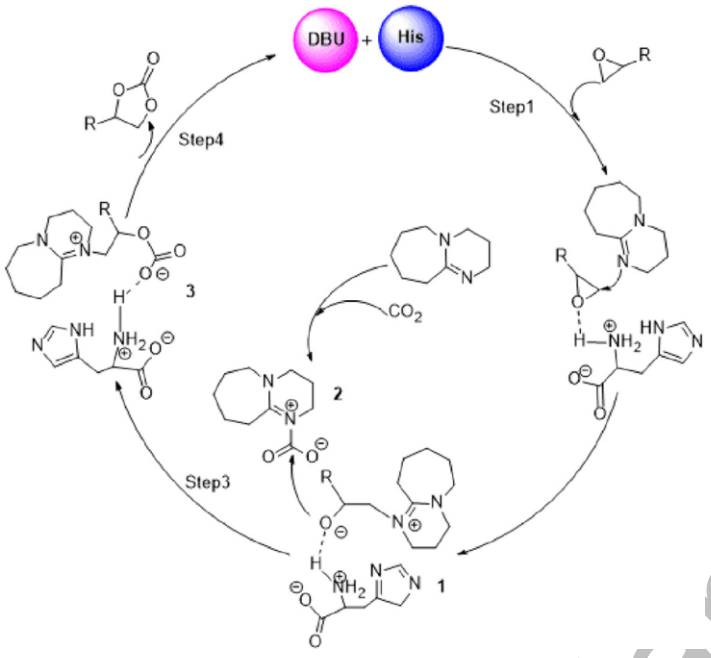


Figure 1. Dependence of PO conversion and PC selectivity on reaction temperature.

Reaction conditions: PO (1 mL), L-histidine (2% mol), DBU (10% mol), CO_2 pressure (2.0 MPa), 2 h.

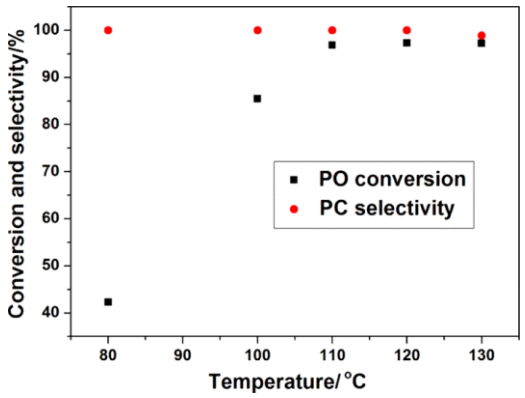


Figure 2. Dependence of PO conversion and PC selectivity on reaction pressure. Reaction conditions: PO (1 mL), L-histidine (2% mol), DBU (10% mol), 2 h, 120 °C.

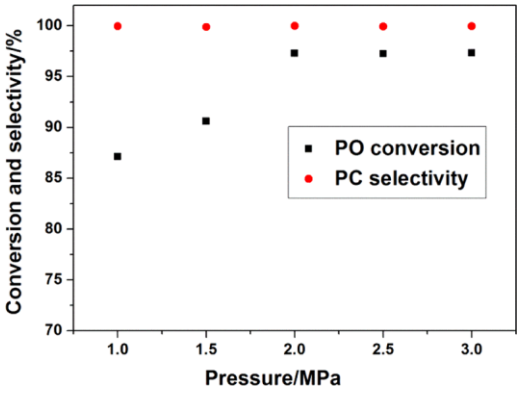


Figure 3. Dependence of PO conversion and PC selectivity on reaction time. Reaction conditions: PO (1 mL), L-histidine (2% mol), DBU (10% mol), CO_2 pressure (2.0 MPa), 120 °C.