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ARTICLE

Natural amino acids/H₂O as metal- and halide-free catalyst system for the synthesis of propylene carbonate from propylene oxide and CO₂ under moderate conditions

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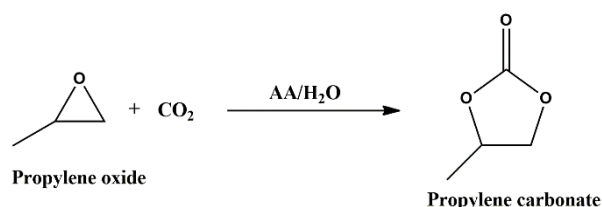
An environmentally clean, binary catalytic system of naturally occurring α -amino acids (AAs)/H₂O has been found to deliver promising yields of propylene carbonate (PC) from propylene oxide (PO) and CO₂ under moderate reaction conditions. Among the various AA systems tested, the highest yield of PC from PO-CO₂ coupling was achieved with the L-His/H₂O system, associated with the basic nature of L-histidine. The effect of various reaction parameters such as the catalyst loading, temperature, CO₂ pressure, and time were evaluated. A plausible reaction mechanism involving synergistic interplay between the –OH groups of H₂O and the COO[–] end of the zwitterionic L-His and the amine moiety of the imidazole ring of L-His was proposed. The process presented herein represents a low cost, ecologically safe, and efficient route with simple work-up employing readily available materials for chemical fixation of CO₂ into high-value chemicals.

Introduction

Transformation of CO₂ into useful organic chemicals has continued to gain prominence based on the environmental and chemical significance. Insertion of CO₂ into oxiranes is a feasible industrial carbon conversion technique,¹ not just on the basis of the 100% atom utilization of the reaction, but also because the cyclic carbonate products have found general applications as aprotic high-boiling polar solvents, electrolytes for lithium-ion batteries, precursors of polymeric materials, and fine chemical intermediates.² A wide range of catalysts such as alkali metal salts, metal oxides, metal complexes, organophosphorous compounds, organic bases, organometallic compounds, and diverse homogeneous and heterogeneous ionic liquids (ILs) have been developed for this coupling reaction.³ The aforementioned catalysts that possess metal acidic centers or strong nucleophilic anion groups exhibited good catalytic activity for the synthesis of cyclic carbonates from CO₂ and oxiranes.

Recent studies, including our own, demonstrated that catalysts bearing functional groups capable of hydrogen bonding, such as hydroxyl, carboxyl, amine etc., exhibited enhanced catalytic activity by synergistic interplay with strongly nucleophilic ions such as Br[–] and I[–].⁴ Even though extensive research has been carried out with

consequently rapid advancement of catalytic systems for the synthesis of cyclic carbonates from CO₂ and oxiranes, the development of a metal- and halide-free catalyst system is still desirable from the environmental perspective. Recently, Sun et al. reported a metal- and halide-free cellulose/superbase catalyst system for the synthesis of cyclic carbonates from CO₂ and oxiranes; however, this system required the use of a strong base such as DBU.^{4p} Similarly, CO₂ adducts of *N*-heterocyclic carbenes^{4q} and alkanolamines^{4r} (our group) have also been reported to serve as metal- and halide-free catalysts for the synthesis of cyclic carbonates from CO₂ and oxiranes. In this context, utilization of natural amino acids (AAs) enriched with chemically reactive acidic and basic sites could be a prime prospect for metal- and halide-free catalysts for the cycloaddition reaction. To date, there are few studies (including ours) related to application of AA-based catalyst systems to the cycloaddition reaction.^{4k,5} Among the existing reports, only two have employed only AAs for the CO₂ cycloaddition with oxiranes, and these required harsh reaction conditions to obtain good conversion.^{5a,b} Herein, we endeavor to exploit the zwitterionic behavior of AAs by employing the AA/H₂O catalytic system (metal- and halide-free) for the solvent-less synthesis of propylene carbonate (PC) from propylene oxide (PO) and CO₂ under moderate reaction conditions (Scheme 1).



Scheme 1 Cycloaddition of PO and CO₂ using L-His/H₂O catalyst system

Results and Discussion

Catalytic activity of AAs

Twenty common naturally occurring α -AAs combined with H₂O were screened for the solvent-less coupling of CO₂ with PO and the results are shown in Table 1. When each of the 20 α -AAs was used alone at 120 °C under 1.2 MPa of CO₂ pressure for 3 h, no product was obtained (entry 1). However, previous studies have reported achieving good catalytic activity for the PO-CO₂ cycloaddition using AAs alone, but only under harsh reaction conditions and over a prolonged period of 48 h (Table S1, Supplementary Information). Interestingly, the combination of AA and H₂O was found to catalyze the PO-CO₂ cycloaddition under moderate reaction conditions (120 °C, 1.2 MPa of CO₂ pressure, and 3 h) (Table 1, entries 2-21). The capability of hydroxyl molecules to synergistically enhance the CO₂-oxirane cycloaddition due to hydrogen bonding is recognized and has been theoretically and experimentally verified by various groups including the current group.⁴ From all the entries in Table 1, it is clear that basic AAs such as L-histidine (L-His) (entry 20), L-lysine (entry 21), and L-arginine (entry 19) showed considerably good activity for conversion of propylene oxide, with respective percentage conversions of 90%, 63%, and 57%. In contrast, acidic AAs like L-aspartic acid (entry 17) and L-glutamic acid (entry 18) exhibited the lowest catalytic activity. The high catalytic activity of the basic AAs compared to the acidic AAs can be ascribed to the presence of additional amine moieties in the side chains of the former.^{5h} Among the evaluated AAs, the best catalytic activity was achieved with basic L-His (entry 20) possessing a nucleophilic –NH group containing a heterocyclic ring (conversion = 90%, selectivity = 91%). Numerous studies^{4c,m,n,p,5h} have reported interaction of the nucleophilic –NH moiety with the non-reactive CO₂ molecules with consequent actuation of the latter to form a carbamate salt along with the synergistic hydrogen bonding influence of the H₂O molecule to activate the –O atom of the oxirane leading to the ring opening reaction. Similar to L-His, AAs possessing a heterocyclic ring, e.g., L-proline (entry 7) and L-tryptophan (entry 9), also showed comparably good activity. In all cases, the only side product obtained during PC formation was propylene glycol.

Table 1. Coupling of PO with CO₂ catalyzed by various α -amino acids/H₂O

Entry	Amino acids	Conversion (%)	Selectivity (%)
1 ^a	AA	-	-
2	glycine	11	70
3	L-alanine	10	72
4	L-leucine	21	75
5	L-isoleucine	13	73
6	L-valine	10	69
7	L-proline	54	86
8	L-phenylalanine	23	79
9	L-tryptophan	26	81
10	L-methionine	24	78
11	L-asparagine	9	74
12	L-glutamine	7	71
13	L-cysteine	9	75
14	L-serine	11	78
15	L-threonine	12	71
16	L-tyrosine	19	73
17	L-aspartic acid	7	79
18	L-glutamic acid	3	73
19	L-arginine	57	81
20	L-histidine	90	91
21	L-lysine	63	84

Reaction conditions: PO = 42.9 mmol, AA amount = 0.19 mmol, H₂O = 5.5 mmol, CO₂ pressure = 1.2 MPa, temperature = 120 °C, time = 3 h. a = without H₂O.

Effect of reaction parameters

Based on the highest catalytic activity of L-His in PC synthesis demonstrated above, this AA was selected for further PO-CO₂ cycloaddition reactions using the L-His/H₂O catalyst system. Figure 1 illustrates the dependence of the conversion of PO on the concentration of L-His. Keeping the reaction conditions constant (5.5 mmol of H₂O, 120 °C, 1.2 MPa of CO₂ pressure, and 3 h), the L-His loading was increased from 0.06 to 0.19 mmol, leading to a corresponding increase in the catalytic conversion from 53% to 90%. Further increment of the concentration of L-His did not bring about any significant enhancement of the conversion, probably due to the presence of excess AA that resulted in restricted dispersion in the reaction

mixture, which eventually limited mass transfer between the active sites and the reactants.^{6a} Similarly, the concentration of

improper mixing of the reactants due to phase separation as evidenced by the insignificant change in conversion under

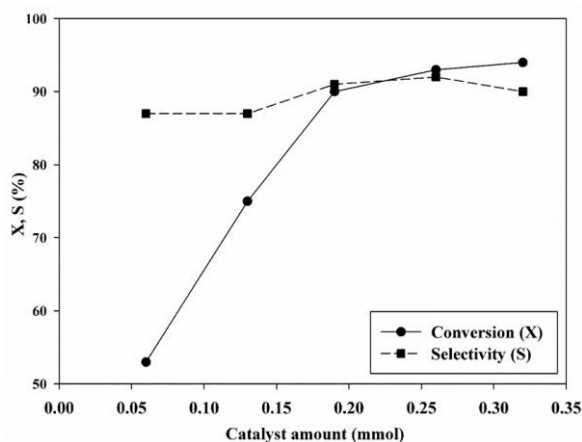


Fig. 1. Dependence of PO conversion on L-His catalyst amount

Reaction conditions: PO = 42.9 mmol, H₂O = 5.5 mmol, temperature = 120 °C, P_{CO₂} = 1.2 MPa, time = 3 h.

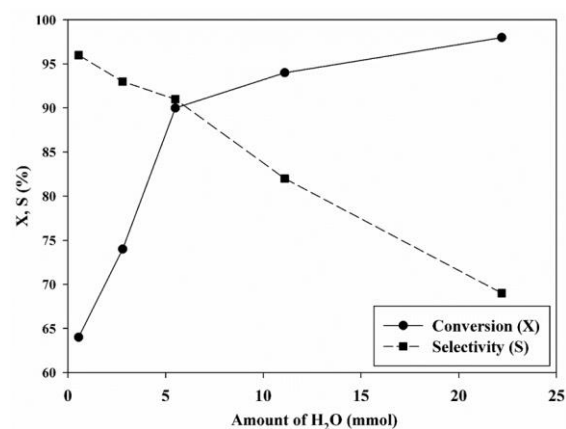


Fig.2 Effect of concentration of H₂O for the PO conversion

Reaction conditions: PO = 42.9 mmol, L-His = 0.19 mmol, temperature = 120 °C, P_{CO₂} = 1.2 MPa, time = 3 h.

H₂O was also varied to evaluate the impact on PC synthesis as depicted in Fig. 2. Upon increasing the amount of H₂O from 0.55 mmol to 5.5 mmol, the conversion increased from 64 to 90%. However, there was a concurrent decrease in the PC selectivity from 96 to 91%. Further increasing the concentration of H₂O to 22.2 mmol improved the conversion to 98%, whereas the selectivity dropped to 69%. This is due to the increased possibility of hydrolysis of PO with increased amounts of H₂O to form the side product (propylene glycol). Hence, 5.5 mmol of H₂O was found to be effective for maximizing the propylene carbonate yield.

The dependence of the cycloaddition reaction of CO₂ and PO on temperature is summarized in Fig. 3. The reaction temperature had a remarkable effect on the catalytic activity of the AA/H₂O system for PO-CO₂ cycloaddition. The conversion of PO increased significantly with increment of the reaction temperature. The conversion of PO increased from 21% at 80 °C to 90% at 120 °C, whereas the selectivity was almost invariable. No additional improvement in the conversion was derived from further increment of the temperature, possibly due to the lower dissolution of CO₂ at higher temperature leading to an insufficient supply of CO₂ molecules for cycloaddition to PO.^{6b} Similarly, the effect of CO₂ pressure on the conversion of PO was evaluated. As illustrated in Fig. 4, variation of the CO₂ pressure from 0.3 to 1.2 MPa induced a continuous increase in the conversion to reach 90% at 1.2 MPa of CO₂ pressure. This could be due to an increase in the CO₂ concentration in the liquid phase of the reaction system at higher CO₂ pressure. Increasing the CO₂ pressure beyond 1.2 MPa possibly lowered the epoxide concentration in the vicinity of the catalyst or resulted in

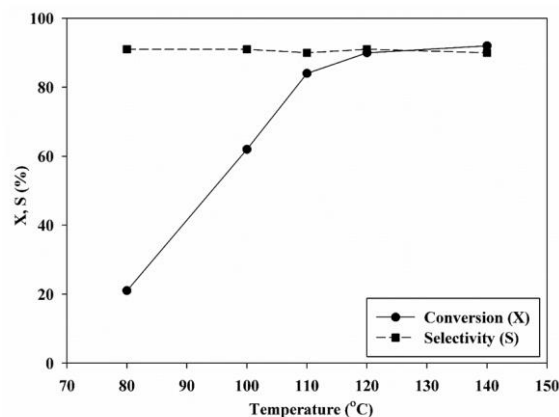


Fig.3 Effect of temperature on the reactivity of L-His/H₂O for the synthesis of PC

Reaction conditions: PO = 42.9 mmol, L-His = 0.19 mmol, H₂O = 5.5 mmol, P_{CO₂} = 1.2 MPa, time = 3 h.

increased pressure conditions.^{6c} The reaction time also had a prominent influence on the catalytic activity of the AA/H₂O system for the synthesis of PC as demonstrated in Fig. 5. A PO conversion of 44% was achieved in the first hour and approached 90% in 3 h and thereafter remained same. The selectivity of PC remained above 90% throughout the entire reaction time.

Overall, 0.19 mmol of L-His, 5.5 mmol of H₂O, 120 °C, 1.2 MPa CO₂, and a reaction time of 3 h were the optimal reaction

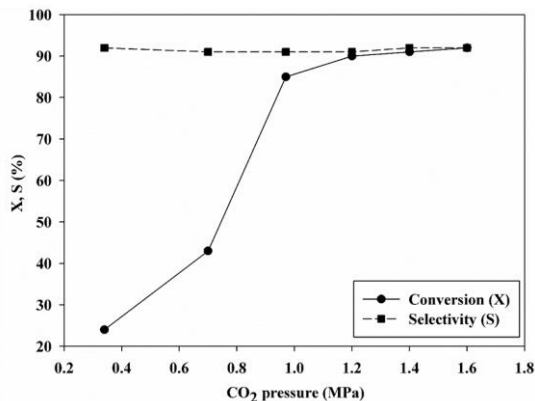


Fig.4 Effect of CO₂ pressure on the reactivity of L-His/H₂O for the synthesis of PC

Reaction conditions: PO = 42.9 mmol, L-His = 0.19 mmol, H₂O = 5.5 mmol, temperature = 120 °C, time = 3 h.

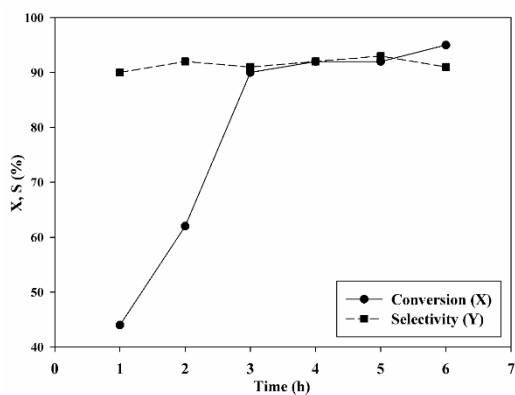


Fig. 5. Effect of reaction time on the reactivity of L-His/H₂O for the synthesis of PC




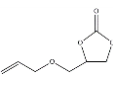

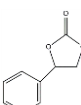

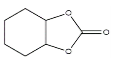
Reaction conditions: PO = 42.9 mmol, L-His = 0.19 mmol, H₂O = 5.5 mmol, temperature = 120 °C, P_{CO₂} = 1.2 MPa.

conditions for the L-His/H₂O catalyzed PO-CO₂ cycloaddition, giving rise to good conversion of 90% and selectivity of 91%.

Conversion of CO₂ with other substrates

In order to evaluate the adaptability of the catalyst system to different oxiranes, various oxirane substrates were used for CO conversion under the optimized reaction conditions in the presence of L-His/H₂O in order to synthesize the corresponding cyclic carbonates; the results are summarized in Table 2. High conversion was achieved with all of the evaluated oxiranes, with the exception of cyclohexene oxide (entry 4); this exception might be due to the high steric hindrance caused by the cyclohexene ring.⁷ When styrene oxide (entry 3) was used, the conversion was slightly lower than achieved with other monosubstituted terminal oxiranes, which is plausibly attributed to the low reactivity of the β-carbon atom of styrene oxide.^{4o}

Table 2. Cycloaddition of CO₂ and various epoxides with AA/H₂O catalyst system

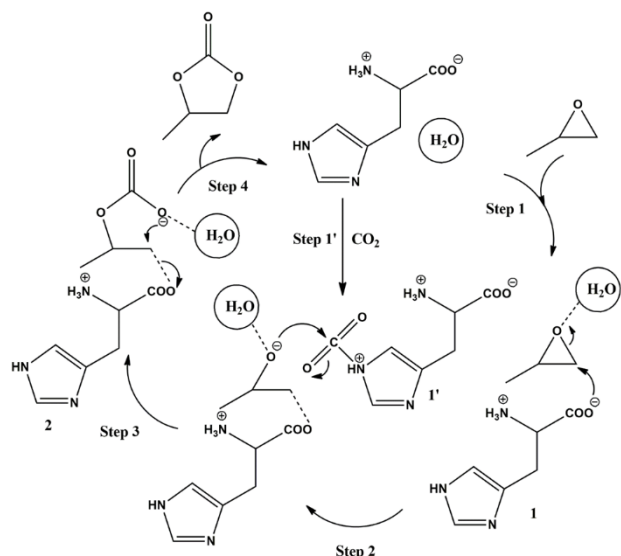
Entry	Epoxide	Cyclic carbonate	Conversion (%)	Selectivity (%)
1			90	91
2			90	85
3			78	82
4			11	90

Reaction conditions: PO = 42.9 mmol, AA amount = 0.19 mmol, H₂O = 5.5 mmol, CO₂ pressure = 1.2 MPa, temperature = 120 °C, time = 3 h.

Possible mechanism for CO₂-PO cycloaddition

Based on the experimental results and previous reports, a proposed mechanism for chemical fixation of CO₂ into cyclic carbonate catalyzed by the L-His/H₂O system is presented in Scheme 2.^{4,5} In Step 1, the H₂O molecule forms a hydrogen bond with the oxygen atom of PO resulting in activation of the oxirane ring. Subsequently, the COO⁻ region of the zwitterionic L-His undergoes nucleophilic attack on the less sterically hindered carbon atom of the oxirane ring creating the ring-opened

intermediate **1**. Analogously (Step 1'), the amine moiety of the imidazole ring of another L-His interacts with the electrophilic carbon atom of the CO₂ molecule to furnish the carbamate salt **1'**. In Step 2, the intermediate **1** undergoes nucleophilic attack on the carbamate salt **1'**, and Step 3 results in the formation of a new alkyl carbonate compound **2**. In the final Step 4, the cyclic carbonate is obtained by intramolecular ring closure. Here, the synergistic influence of the hydrogen bonding capability of the H₂O molecule in activating the oxirane ring, nucleophilic attack on the least hindered carbon atom of the oxirane ring by the COO⁻ region of the zwitterionic L-His, and the formation of a carbamate salt by the amine moiety of the imidazole ring of L-His interacting with the electrophilic carbon atom of the CO₂ molecule cooperatively result in the formation of the final cyclic carbonate.



Scheme 2 Proposed mechanism of L-His/H₂O mediated cycloaddition

Conclusions

In summary, respective systems of twenty naturally occurring α -AAs combined with H₂O were catalytically screened for the metal- and halide-free coupling of CO₂ with PO. Among the various AAs, the L-His/H₂O system employing a basic AA was found to be the most active and gave rise to the maximum conversion of 90% with 91% selectivity. From evaluation of the various reaction parameters such as the catalyst loading, temperature, CO₂ pressure, and time it was found that 0.19 mmol of L-His combined with 5.5 mmol of H₂O at 120 °C using a CO₂ pressure of 1.2 MPa for a duration of 3 h were the optimal

conditions for maximizing the PO conversion. The L-His/H₂O catalyst system was found to be applicable to other mono-substituted and disubstituted oxiranes. A possible mechanism for the synthesis of PC has been demonstrated, in which the hydrogen bonding capability of the H₂O molecule that activates the oxirane ring of PO, nucleophilic attack by the COO⁻ region of the zwitterionic L-His on the carbon atom of PO, and carbamate formation by the amine moiety of the imidazole ring of L-His with the carbon atom of the CO₂ molecule resulted in synergistic activation of PO and CO₂ with consequent enhancement of the catalytic activity of the system. Despite the numerous catalysts that have been developed for the cycloaddition of oxirane and CO₂, the current metal- and halide-free catalyst system (AA/H₂O) for the solvent-less synthesis of cyclic carbonates under moderate reaction conditions is demarcated by various advantages such as environmental friendliness, the simple work-up process, easy availability of materials, low cost, etc.

Experimental

Materials

L-histidine (>99%) (L-His), and other amino acids were purchased from Aldrich and used without further purification. Propylene oxide (PO) and other oxiranes were purchased from Aldrich and used as received. Carbon dioxide of 99.999% purity was used without further purification.

Cycloaddition of PO and CO₂

Synthesis of propylene carbonate (PC) from PO and CO₂ using the L-His/H₂O catalyst system (Scheme 1) was performed in a 50 mL stainless-steel autoclave equipped with a magnetic stirrer. For each typical batch operation, PO (42.9 mmol) and L-His/H₂O were charged into the reactor. The reactor was then purged several times with CO₂ and pressurized with CO₂ to a preset pressure of 0.3–1.6 MPa at room temperature. The reactor was then heated to the desired temperature, and the reaction was initiated by stirring the reaction mixture at 600 rpm. After the reaction time elapsed, cycloaddition was stopped by cooling the reaction mixture to 0 °C, and the products were identified by means of a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 μ m) using a flame ionization detector. The product yield was determined using an internal standard method with biphenyl (0.05 g) as the standard.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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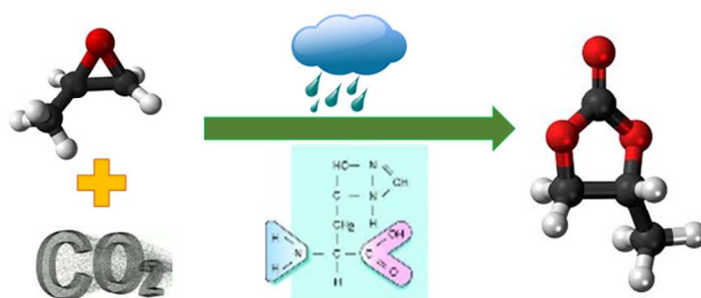
Natural amino acids/H₂O as metal- and halide-free catalyst system for the synthesis of propylene carbonate from propylene oxide and CO₂ under moderate conditions

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Amino acid/H₂O catalytic system (metal- and halide-free) for the synthesis of propylene carbonate from propylene oxide and CO₂