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Microwave-assisted one pot-synthesis of amino acid ionic liquids in water: simple catalysts for styrene carbonate synthesis under atmospheric pressure of CO_2

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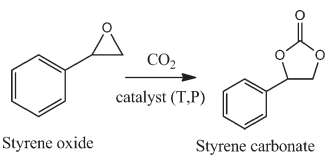
A novel variety of ionic liquids based on naturally occurring amino acids is expeditiously synthesized in water using microwave energy. The amino acid ionic liquids (AAILs) exhibit eminent catalytic activities towards the synthesis of styrene carbonate from styrene oxide and carbon dioxide at atmospheric pressure. The synergistic interaction of the hydrogen-bonding groups with the nucleophile in the AAIL is believed to be the key factor behind the catalytic cycloaddition. Among the various kinds of AAILs tested, the basic AAILs were found to be the most efficient owing to the presence of extra amino groups that could activate the carbon dioxide molecule by formation of a carbamate salt. The AAILs showed appreciable reusability over four cycles without compromising the selectivity towards styrene carbonate synthesis and hence represents an easily synthesizable series of eco-friendly catalysts for CO_2 fixation.

Introduction

The relevance of an effective mitigation of excess CO_2 from the environment is undoubtedly clear to the scientific community around the globe because of CO_2's obvious detrimental impact on the environment. The direct sequestration of CO_2 such as by carbon capture and storage (CCS) techniques, employed directly from industrial emission outlets to underground aquifer sinks, is a widely practiced methodology adopted for addressing the exponential increase in atmospheric CO_2 concentrations. However, the physico-chemical properties of CO_2, such as its non-toxicity, non-flammability, ease of storage, and abundant nature, evoked a new window of chemical explorations for its utilization, whereby serious and dynamic research has been devoted to the successful transformation of CO_2 into valuable industrial products. Although currently the mitigation of CO_2 emissions by this route is limited, the employment of CO_2 as a C_1 feedstock could replace the currently employed hazardous C_1 materials such as $COCl_2$ and CO in a large number of organic transformations. Cyclic carbonates, synthesized by the cycloaddition of epoxides and CO_2 (Scheme 1), are excellent aprotic solvents with low odor and toxicity and have been employed as electrolytic solvents for lithium-ion batteries and monomers for polymer synthesis.[1a–e,2]



Scheme 1 Synthesis of styrene carbonate.

Of the many catalytic systems deployed, ionic liquids[3a–h] and metal complex systems[4a–d] stand out as the most distinguished and promising tailor-made, task-specific catalysts. This description of ionic liquids is attributed to the ease of tunability of their physical and chemical properties by a meticulous choice of cationic and anionic species. However, the definition of ionic liquids is quite ambiguous; they are neoteric solvents with green properties such as non-volatility, liquidity over a wide range of temperatures, high thermal stability, and incombustibility. The typical formulation of an ionic liquid catalyst includes quaternary ammonium, imidazolium, pyridinium, and phosphonium cations, as well as a wide variety of anions such as halides, hexafluorophosphates, tetrafluroborates, and nitrates, and these have been intensively studied for their potential towards CO_2–epoxide cycloaddition.[3a–g] Various experimental and theoretical studies have shown that ionic liquids with strongly nucleophilic anions, in association with hydroxyl and carboxylic groups, furnish a better yield of cyclic carbonates by means of playing a synergistic role. Hence, there

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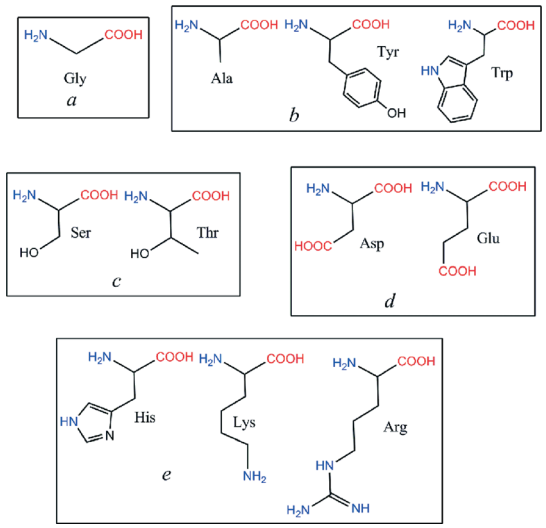
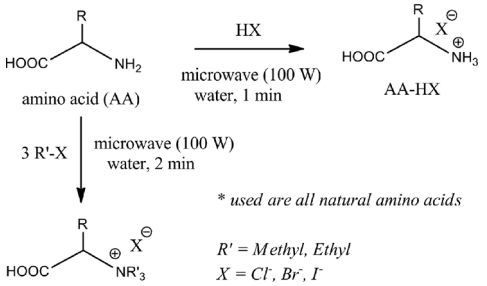
has been a growing interest in the rational design and synthesis of ionic liquids equipped with hydrogen-bonding groups from various starting materials such as alkylimidazoles, followed by the post-synthetic tethering of hydroxyl and/or carboxylic moieties to these ionic liquids.[3b,3g] However, the claim of ionic liquids to be fully "green" is still open to debate since the relative abundance and non-toxicity of the starting materials is a pre-requisite for green chemistry. Recently, bio-renewable materials such as lactates, sugar substitutes, and amino acids have been identified as ideal precursors for ILs from both economical and environmental perspectives.[5a–p] These attempts tend to capitalize the potential design capacity of the biological materials for the development of task-specific eco-friendly ILs.

In this context, utilization of natural amino acids (AA) as ionic liquid precursors (Scheme 2) becomes the crescendo of designer ionic liquid synthesis, since AA represent one of the most versatile class of natural, bio-renewable, and non-toxic raw materials from nature's toolbox. The additional advantage of amino acid ILs (AAILs) is the presence of multiple hydrogen-bonding groups, which eliminates the need for post-synthetic covalent tethering of functional moieties. By virtue of their excellent and easy tunability, amino acids can make a direct contribution to the search for 'greener' solvents with desirable physicochemical properties.

According to the tenets of 'green' chemistry, the efficiency of a chemical synthesis is not only evaluated on the basis of the abundance and non-toxicity of the raw material, but the reaction time, energy requirement, and the protocols involved are also critically monitored. Recently, the ability of aqueous microwave chemistry to induce organic transformations has attracted increased interest owing to reduced reaction times, lower environmental impact, and minimal formation of side products.[5a–g] Since dielectric heating of polar molecules is the key to efficient microwave heating, water is the best solvent for microwave-assisted chemical



Scheme 2 Amino acid precursors.



Scheme 3 Synthesis of amino acid ionic liquids.

reactions. A number of studies have already reported the use of microwaves for ionic liquid synthesis in solvent-free and aqueous media.[5f,6g] The capacity of ionic environments to generate internal pressure and promote the interaction of reactants in solvent cavities renders the use of microwave energy for ionic liquid synthesis an expeditious approach. Hence, we have attempted the one-pot synthesis of cationic AAILs in water using microwave energy for time spans as short as 2 minutes (Scheme 3). We have also investigated the catalytic activity of these AAILs towards the cycloaddition of CO_2 to styrene oxide at atmospheric pressure.

Results and discussion

Until now, the two approaches adopted for the synthesis of AAILs have used amino acids either as anions of commercially available IL cations such as alkyl imidazolium[5b–d] or as cations by means of simple acidification followed by metathesis with different anions.[5e–h] Most work has focused on the former approach, wherein nearly all the natural amino acids have been successfully converted into anionic species, whose physicochemical properties have been studied. In particular, a few works demonstrated the possibility of using amino acids as cation centers for a wide variety of anions that were successfully used as chiral ligands in chiral ligand-exchange capillary electrophoresis and as catalysts for Diels–Alder type reactions,[5f] *etc.* With respect to CO_2 fixation, Gong *et al.*[5g] successfully developed an L-proline-based ionic liquid under reflux conditions in acetonitrile for 48 h and they efficiently catalyzed the synthesis of cyclic carbonates under atmospheric pressures of CO_2 within 24 h. Most recently, our group[7a] has theoretically proposed and experimentally validated the synergistic catalytic activity of the iodide nucleophiles and –COOH entities of the quaternized glycine catalyst in the CO_2–epoxide cycloaddition, *via* density functional calculations. A similar betaine system[7b] was also found to be an effective catalyst in cyclic carbonate synthesis under moderate reaction conditions. However, a systematic study of the catalytic behaviors of other cationic AAILs in the CO_2–epoxide cycloaddition remains underexplored, despite the fact that amino acids are the monomer units of the most efficient biological catalysts, the enzymes.

Since natural amino acids exhibit diverse chemistries by virtue of their different side-chain functionalities and

hydrogen-bonding groups, we deemed it worthwhile to investigate the catalytic ability of various AAILs based on their molecular structure. Assuming glycine (a) to be the standard amino acid, (by virtue of its simple structure and small size) the other amino acid (AA) precursors were classified into four groups: (b) AAs with hydrophobic side chains, (c) AAs with polar uncharged side chains, (d) acidic and (e) basic (Scheme 2). These AAILs were easily synthesized in water by means of acidification with HI in a one-pot synthetic procedure using microwave energy in 2 minutes (Scheme 3). The catalytic behavior of the AAILs towards the cycloaddition of styrene oxide to carbon dioxide is shown in Table 1. All the reactions were carried out at 120 °C for 6 h under solvent free conditions. No product (styrene carbonate) was detected in the absence of a catalyst (entry 1). Neither glycine (entry 2) nor HI (entry 3) resulted in a conversion higher than 5% when used alone under the employed reaction conditions. However, the amino acid ionic liquid Gly–HI (entry 4) achieved a conversion of 34% with selectivity for styrene carbonate (SC) in excess of 97% under atmospheric pressure of CO_2. This reaction demonstrated the synergistic catalytic activities of the hydrogen-bonding groups and the anion of the AAIL. The three AAILs that had different hydrophobic side chains (Trp, Tyr, Ala) resulted in different conversion rates of SO under the same reaction conditions. While Ala–HI exhibited a SO conversion of 29% (entry 5), Tyr–HI that possessed a hydroxyl group in the side chain resulted in 52% conversion (entry 6), and the –NH containing Trp–HI produced even better conversion of 73% (entry 7). The hydroxyl-containing polar uncharged side chain AAILs, Ser–HI and Thr–HI achieved respective conversions of 61% and 52% (entries 8 and 9). The acidic AAILs, *i.e.*, Asp–HI, and Glu–HI, also resulted higher conversion rates of SO with high selectivities (entries 10 and 11). All the basic AAILs afforded a relatively higher SO conversion (more than 70%), with His–HI being the most effective catalyst. While Lys–HI (entry 12) and Arg–HI (entry 13) exhibited 79% and 70% SO conversion, respectively, His–HI (entry 14) exhibited a SO conversion of almost 92% (TON = 328), maintaining the high selectivity induced by other AAILs. All the above AAILs maintained selectivities of more than 97%. The fact that hydrogen-bonding entities can accelerate epoxide conversion is consistent with the obtained results (entries 4 and 5 *vs.* 6, 8 and 9). The increased catalytic activities of Ser–HI (entry 8) and Thr–HI (entry 9) and the acidic AAILs (entries 10 and 11) that contained additional –OH and –COOH groups, respectively, also corroborated the active catalytic role of hydrogen-bonding groups of AAILs in the SO–CO_2 cycloaddition. To the best of our knowledge, this is the highest catalytic activity exhibited by any AAIL in a CO_2–epoxide cycloaddition under the employed reaction conditions. The previously reported proline-based ionic liquid[5g] exhibited a SO conversion of >77% (TON = 84) only with triethylamine as co-catalyst (1 mol% catalyst, 90 °C, 1 atm CO_2, 24 h), whereas the proline ionic liquid alone yielded only 12% SO conversion. Although a direct comparison between the various efficient ionic liquids for cyclic carbonate synthesis is tedious owing to the differences in the reaction conditions, we noticed that

Table 1 Catalytic test runs towards synthesis of styrene carbonate from styrene oxide and CO_2[a]

	Catalyst	Conversion[b] (%)	Selectivity[b] (%)	TON
1	None	—	—	—
2[c]	Gly	—	—	—
3	HI	3	81	10
4[c]	Gly–HI	34	97	121
5[d]	Ala–HI	29	98	103
6[d]	Tyr–HI	52	97	185
7[d]	Trp–HI	73	99	260
8[d]	Ser–HI	61	98	217
9[e]	Thr–HI	52	98	185
10[e]	Asp–HI	42	93	149
11[f]	Glu–HI	49	95	175
12[f]	Lys–HI	79	97	282
13[g]	Arg–HI	70	98	250
14[g]	His-HI	92	99	328
15[h]	CBImBr[3h]	96	98	63
16[i]	HEMImBr[3b]	99	99	62
17[j]	$Pro_{4,4}Br/Et_3N$[5g]	79	98	84
18[k]	$[(salen)Al]_2O/Bu_4NBr$[4b]	64	—	24.8
19[l]	Zn–salphen complex–2/Bu_4NBr[4c]	66	—	26.4
20[m]	Al–cat–1/Bu_4NBr[4d]	99	96	1980

[a] Catalyst amount: 0.1 mmol (0.28 mol%), 35 mmol SO, 120 °C, 0.1 MPa, 6 h. [b] From GC using toluene as internal standard (side product is styrene-1,2-diol). [c] AAIL synthesized from neutral amino acid. [d] AAIL synthesized from neutral amino acid with hydrophobic amino acid chain. [e] AAIL synthesized from neutral amino acid with polar side chain. [f] AAIL synthesized from acidic amino acid. [g] AAIL synthesized from basic amino acid. [h] AAIL synthesized from 1.5 mol%, 120 °C, 1.3 MPa, 2 h. [i] AAIL synthesized from 1.6 mol%, 125 °C, 2 MPa, 1 h. [j] AAIL synthesized from 1 mol%, 90 °C, 0.1 MPa, 24 h. [k] AAIL synthesized from 2.5 mol%, co-catalyst 2.5 mol%, 25 °C, 0.1 MPa, 3 h. [l] AAIL synthesized from 2.5 mol%, co-catalyst 1 mol%, 45 °C, 1 MPa, 18 h, 5 mL CH_2Cl_2. [m] AAIL synthesized from 0.05 mol%, co-catalyst 0.25 mol%, 70 °C, 10 MPa, 18 h, 0.5 MEK (methylethylketone) co-solvent.

AAILs furnished higher TON values compared to the other ionic liquid systems with hydrogen bonding functionalities (Table 1, entry 14 *vs.* 15 and 16). However, these organocatalysts were inferior to the inorganic metal complexes, which excelled in their activities under very mild reactions (Table 1, entry 18, 19, and 20).

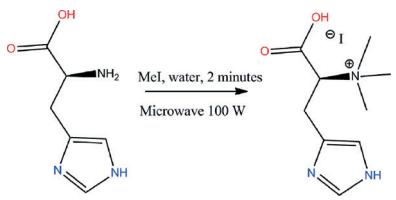
The probable reason for the higher catalytic activities of basic AAILs compared to those of acidic AAILs can be attributed to the presence of additional amine moieties in the side chains of basic AAILs. While the –COOH groups and –OH groups of the catalytic species are believed to activate the epoxide –O atom towards the ring opening reaction,[8a–k] the nucleophilic –NH groups are thought to have an increased ability to interact with the non-reactive CO_2 molecules. The fact that aqueous alkyl amine solutions are industrially employed as CO_2-absorbing agents corroborates the concept that the –NH moiety effectively forms a carbamate salt by means of a nucleophilic attack on the carbon atom of the carbon dioxide, which results in the activation of the otherwise non-reactive CO_2 molecule.

Since His–HI exhibited the highest catalytic activity in SC synthesis, we extended the histidine-based AAIL synthesis by using methyl and ethyl iodide in aqueous media in a microwave reactor (Scheme 4). Table 2 lists the catalytic activities exhibited by the His–MeI and His–EtI ionic liquids during SC synthesis under solvent-free conditions. The activity with methyl and ethyl substituted histidine ionic liquids wasn't much different. To gather insight into the role of anions, chloride and bromide-possessing histidine ionic liquids similar to His–HI were synthesized and the catalytic activity of these ionic liquids are shown in Table 2, entries 4 and 5. As is evident from entries 1–3, all the iodide anion-possessing histidine ionic liquids (His–HI, His–MeI, and His–EtI) resulted in extremely high conversion/yields of more than 90%, irrespective of the length of the alkyl chain involved. The reactions were carried out under an atmospheric pressure of CO_2 at 120 °C over 6 h using 0.28 mol% of the catalyst.

Since the catalytic activity exhibited by bromide and chloride-containing histidine ionic liquids was limited to 64% and 27%, respectively (entries 4 and 5), which was significantly lower than the SC yields obtained with histidine ionic liquids that had iodide as the counter anion. This demonstrated the superior ability of the iodide anion to effectuate the synergy with the hydrogen-bonding groups of the amino acid cation compared with the bromide and chloride anions.

Optimization studies carried out with the His–MeI ionic liquid under various experimental conditions of catalyst concentration, temperature, and reaction time are discussed below. Fig. 1 shows the dependence of SO conversion on the amount of His–MeI catalyst. The catalytic activity gradually increased on going from 0.1 mol% to 0.28 mol% of the His–MeI catalyst and reached near-saturation at 0.28 mol% of His–MeI, where the SO conversion reached 95% with 99% SC selectivity.

Temperature also has a very strong influence on the His–MeI catalysis of SO conversion to SC. Fig. 2 shows the increase in the catalytic rate with increasing temperature between 80 °C and 140 °C. An almost negligible yield of SC was obtained at 80 °C; however, the catalytic activity increased exponentially at temperatures above 100 °C, reaching a maximum at 120 °C with 95% SO conversion and SC selectivity in excess of 99%. These results were attributed to the decrease of viscosity of the catalyst system at elevated temperatures, thereby resulting in increased mobility of the active species. This in turn facilitated more effective interactions of the catalyst with the substrate molecules, overcoming the energy barrier of the reaction. Interestingly, the His–MeI system maintained its selectivity even at high temperatures of 140 °C. The dependence of SC yield and selectivity on the reaction time was also evaluated (Fig. 3), where the catalytic activity was found to be optimum at 6 h.



Scheme 4 Synthesis of histidine–MeI ionic liquid (His–MeI).

Table 2 Role of anions and alkyl chains[a]

Entry	Catalyst	SO conversion[b] (%)	SC selectivity[a] (%)
1	His–MeI	95	99
2	His–EtI	92	99
3	His–HI	93	99
4	His–HBr	64	98
5	His–HCl	27	96

[a] Reaction conditions: SO 4 ml (35.02 mmol), catalyst amount 0.1 mmol, 120 °C, 0.1 MPa, 6 h. MeI = methyliodide, EtI = ethyliodide, X = iodide (I), bromide (Br), chloride (C). [b] From GC using toluene as internal standard.

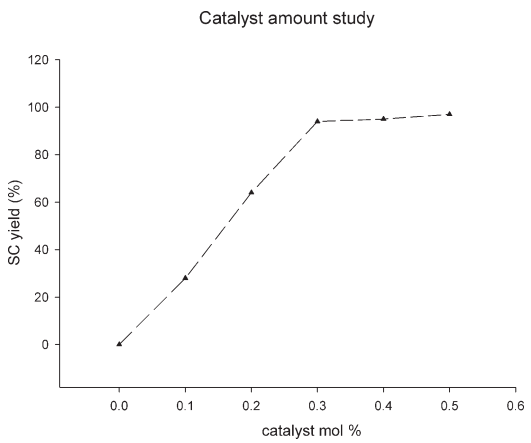


Fig. 1 Dependence of SC yield on catalyst amount. Reaction conditions: SO = 35.5 mmol, 120 °C, 0.1 MPa, 6 h. Selectivity of SC >99%.

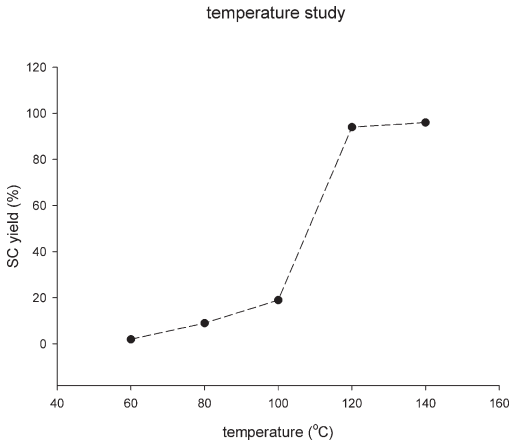


Fig. 2 Effect of temperature in the His–MeI catalyzed cycloaddition. Reaction conditions: SO = 35.5 mmol, cat.amt = 0.28 mol%, 0.1 MPa, 6 h. Selectivity of SC >99%.

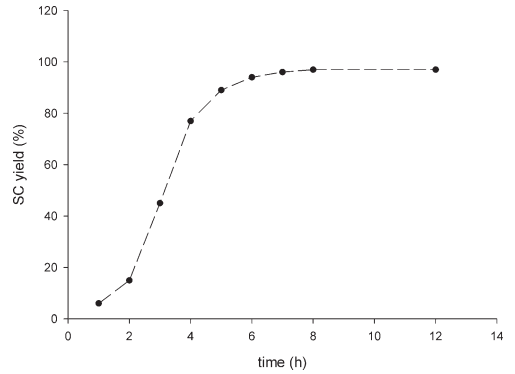


Fig. 3 Time variant study of SC synthesis using His–MeI catalyst systems. Reaction conditions: SO = 35.5 mmol, cat.amt = 0.28 mol%, 120 °C, 0.1 MPa. Selectivity of SC >99%.

Since AAILs are generated in aqueous media, the recovery of the catalyst is easily achieved by separation using water followed by drying at 60 °C for 24 h (vacuum). Gratifyingly, the recovered catalysts exhibit moderately good reusability towards styrene carbonate synthesis under the optimized reaction conditions (Fig. 4). Although the percentage conversion of SO was found to decrease in consecutive cycles during reuse, the selectivity remained almost unchanged (>95%) demonstrating the efficacy of the 'green' catalyst from a renewable source.

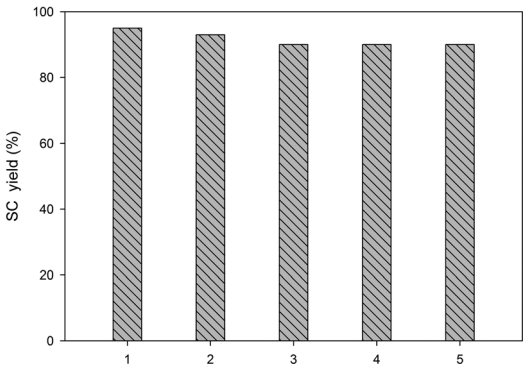
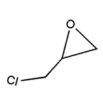
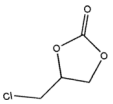
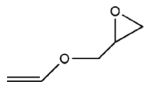
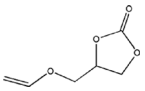
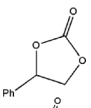
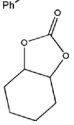


Fig. 4 Reusability performance of His–MeI ionic liquid in SC synthesis, 35.5 mmol SO, 0.28 mol% catalyst, 120 °C, 6 h, 0.1 MPa CO_2.

Trials to find out the pressure dependence of His–MeI mediated catalysis of SO–CO_2 coupling and the catalytic activity towards a few other epoxides led us to some interesting results. While SO efficiently underwent cycloaddition to CO_2 within the pressure range of 0.1 MPa to 1.2 MPa, the cycloaddition tendency of the other epoxides were different. At 120 °C in 6 h with 0.28 mol% of catalyst the reactivity of various epoxides towards cyclic carbonate formation followed the order: styrene oxide ≫ allyl glycidyl ether > propylene oxide > epichlorohydrin ≫ cyclohexene oxide at atmospheric pressures of CO_2 (Table 3). However, with a gradual increase in the CO_2 pressure, the various epoxides responded in different quantities to the coupling reaction such that propylene oxide (entry 3) and allyl glycidyl ether (entry 2) reached higher conversion rates of 81% and 93%, respectively, at 0.6 MPa pressure with very high selectivity towards the corresponding cyclic carbonates. While all the epoxides attained excellent conversion at 1 MPa, the internal epoxide cyclohexene oxide (entry 5) remained hard for effective coupling reaction with CO_2 throughout the entire pressure studies due to its high steric hindrance, a fact well known to the research community.[9a,b] We surmise this difference in cyclic carbonate yield from different epoxide substrates at various pressures to the difference of CO_2 solubility in the corresponding reaction mixtures, which may have directly influenced the rate of carbamate formation. Since styrene oxide gave consistently higher cycloaddition rates throughout the CO_2 pressures applied, CO_2 solubility in SO should be higher than that in other epoxides, even under pressures as low as 1 atmosphere.

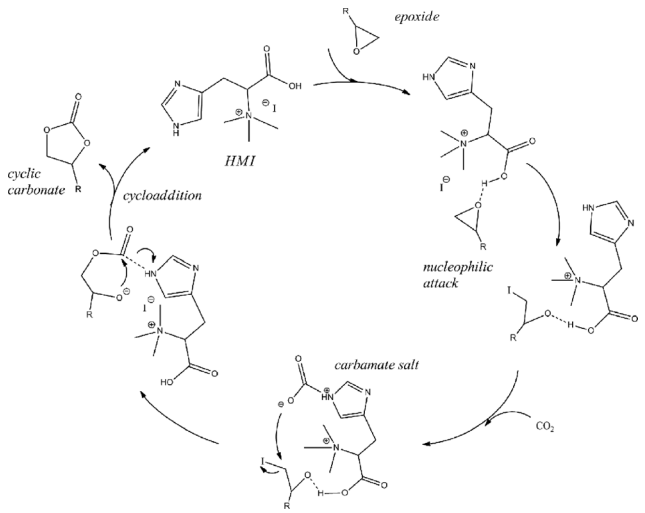
The mechanism of the cycloaddition of CO_2 to epoxides has been studied elaborately previously, both experimentally and theoretically.[8a–k] When this reaction proceeds under the influence of an ionic catalyst, such as an ionic liquid, a nucleophilic attack on the least hindered carbon atom of the epoxide by the anion initiates the reaction, followed by the cycloaddition of CO_2. In this study, neither HI (Table 1, entry 3) nor glycine (Table 1, entry 2) catalyzed the CO_2–epoxide coupling to any significant extent, whereas Gly–HI (entry 4) appreciably catalyzed the reaction, which demonstrated the synergistic interaction of the iodide anion with the hydrogen-bonding groups of the glycine cation. From Table 2, entries 3–5, the anion was found to have a substantial effect on the catalytic rate, as a strongly nucleophilic leaving group (iodide anions) resulted in high SC yields when compared to the other halide ions (bromide and chloride). The comparison between the different kinds of AAILs employed revealed that AAILs with an additional basic moiety produced better yields of cyclic carbonates. The role of –NH groups in activating the CO_2 molecule has been already conclusively reported by several studies.[8d,k] In summary, a plausible mechanism of the His–MeI catalyzed

Table 3 Pressure dependence of various epoxides on cyclic carbonate using His–MeI catalyst[a]

Entry	Epoxide	Product	Product yield[b] (%) at various pressures of CO_2 (MPa) 0.1	0.6	1.0
1			12	71	99
2			56	93	98
3			16	81	99
4			95	98	98
5			—	12	29

[a] His–MeI 0.28 mol%, 35.5 mmol epoxide, 120 °C, 6 h. [b] From GC using toluene as internal standard.

cycloaddition of CO_2 to epoxide is shown in Scheme 5. The –COOH group of the catalyst hydrogen bonds with the oxygen atom of the epoxide, weakening the more probable β C–O bond of the epoxide.[8b,g,h] Then, the iodide nucleophile attacks the β carbon atom and forms a C–I bond. Meanwhile, the electrophilic C atom of the CO_2 molecule interacts with the amine moiety of the imidazole ring to form a carbamate salt.[8d,k] Thereafter, the oxy anion of the carbamate salt attacks the β carbon atom of the epoxide when the iodide anion leaves the loop. Cycloaddition follows this step, producing cyclic carbonate and regenerating the catalyst. It is worthwhile to mention that the α C atom of the epoxide is also prone to undergo the same events as those of the β carbon since the energy barriers do not differ that much.[8l]



Scheme 5 Mechanism of cycloaddition of CO_2 with epoxides using His–MeI catalyst.

Conclusions

We have utilized a simple and efficient method for synthesizing ionic liquids from bio-renewable amino acids using microwave energy and water (reaction time 2 minutes) for the synthesis of styrene carbonate from CO_2 and styrene oxide at atmospheric pressure under solvent-free conditions. All the synthesized AAILs exhibited promising catalytic activity through the synergy between the hydrogen-bonding groups and the nucleophiles of the AAILs. The iodide ion was found to be the most compatible nucleophile for an efficient catalysis. The catalysts displayed appreciable recyclability with respect to styrene oxide conversion and styrene carbonate selectivity. We believe that the development of microwave-assisted approaches that employ the most environmentally benign solvent, water, and very short reaction times meets the requirements of sustainable chemistry for synthesizing task-specific ionic liquids. The facile activation of water molecules using microwaves demonstrates the utility of yet another synergistic approach for the development of eco-compatible methodologies for the synthesis of chemically significant materials such as ionic liquids.

Experimental

All reagents and solvents (except DS water) were pure analytical grade materials purchased from commercial sources (Sigma Aldrich Co. South Korea) and were used without

further purification, unless stated otherwise. CO_2 (99.9%) was obtained from MS Gas Corporation, Korea. A gas chromatograph (HP 6890 A) equipped with a HP-1 capillary column was used to determine the concentration of the various cyclic carbonates formed. The peak of the cyclic carbonate was identified with an authentic sample. The ^{1}H-NMR spectra were recorded in D_2O on a Varian 500 MHz instrument with TMS as an internal standard. DMSO was used as the solvent for ^{13}C-NMR (75 MHz).

Typical procedure for preparation of AAILs

Synthesis of His–HI ionic liquid. 0.1mol of L-histidine was dissolved in 5 ml distilled water. One molar equivalent of HI (55%) was added dropwise. The reaction mixture was irradiated with microwave pulses (100 W) for 2 minutes. The solution turned chrome yellowish and the solid collected using a rotary evaporator. After drying *in vacuo* at 70 °C for 10 h, a pale yellow solid was obtained. All the other AA–HI ionic liquids were synthesized as above. ^{1}H-NMR: δ = 8.34 (s, 3 H), 7.71 (s, 1 H), 7.01 (s, 1 H), 4.1 (t, 1 H), 3.3 (q, 1 H), 3.1 (q, 1 H) ppm. ^{13}C-NMR δ = 174.19, 136.58, 132.47, 117.03, 55.07, 28.43.

Synthesis of histidine–alkyl halide ionic liquid. i) *N*,*N*,*N*-trimethylhistidine iodide (His–MeI). 0.1mol of L-histidine was dissolved in 5 ml distilled water. Three molar equivalents of methyl iodide was added and the reaction mixture was irradiated with microwave pulses (100 W) for 2 minutes. The solution turned pale yellow after a few seconds and rotary evaporation yielded a light yellow viscous fluid. ^{1}H-NMR: δ = 8.26 (s, 1H), 7.69 (s, 1 H), 7.1 (s, 1 H), 4.0 (t, 1 H), 3.3 (q, 1 H), 3.8 (s, 9H), 3.1 (q, 1 H) ppm. ^{13}C-NMR: δ = 172.20, 134.11, 127.92, 118.53, 80.06, 53.07, 25.43.

ii) *N*,*N*,*N*-triethylhistidine iodide (His–EtI) was synthesized by dissolving the L-amino acid (0.1 mmol) in an ethanol/water (1 : 1) mixture followed by the addition of the respective alkyl halide (0.3 mol) and irradiation with microwave (100 W) for 2 minutes. After the reactor was cooled, ether separation was performed. Upon concentration using rotary evaporation, a highly viscous yellow ochre liquid resulted. The liquid was extracted with methanol and concentrated again to yield a pure ionic liquid.

^{1}H-NMR: δ = 8.42 (s, 1H), 7.49 (s, 1H), 7.1 (s, 1 H), 4.0 (t, 1 H), 3.35 (q, 1 H), 3.8 (s, 9H), 3.1 (q, 1 H), 1.1 (t, 9H) ppm. ^{13}C-NMR: δ = 174.60, 136.23, 115.92, 117.53, 77.65, 52.5, 20.43.

NMR spectra of AA–HI ionic liquids

Glycine iodide (Gly–HI). ^{1}H-NMR: δ = 8.13 (s, 3H), 3.63 (s, 2H) ppm. ^{13}C-NMR: δ = 171.05, 41.37 [pale yellow viscous liquid at RT].

L-Alanine iodide (Ala–HI). ^{1}H-NMR: δ = 8.32 (s, 3H), 4.13 (t, 3H) ppm. ^{13}C-NMR: δ = 169.98, 52.32, 20.12 [yellow viscous liquid at RT].

L-Aspartic acid iodide (Asp–HI). ^{1}H-NMR: δ = 8.42 (s, 3H), 4.18 (t, 3H), 2.61(d, 2H) ppm. ^{13}C-NMR: δ = 171.84, 173.14, 38.14, 52.64 [yellow viscous liquid at RT].

L-Glutamic acid (Glu–HI). ^{1}H-NMR: δ = 8.42 (s, 3H), 4.21 (t, 3H), 2.32 (m, 2H), 2.42 (t, 2 H) ppm. ^{13}C-NMR: δ = 169.84, 171.23, 53.61, 31.26, 38.14 [yellow viscous liquid at RT].

L-Serine (Ser–HI). ^{1}H-NMR: δ = 8.45 (s, 3H), 4.17 (t, 3H), 3.83 (d, 2 H) ppm. ^{13}C-NMR: δ = 169.68, 59.52, 52.54 [chrome yellow viscous liquid at RT].

L-Threonine iodide (Thr–HI). ^{1}H-NMR: δ = 8.3 (s, 3H), 4.12 (t, 3H), 3.71 (m, 1H), 1.21 (d, 3H) ppm. ^{13}C-NMR: δ = 169.75, 63.71, 58.56, 20.11 [pale yellow viscous liquid at RT].

L-Lysine iodide (Lys–HI). ^{1}H-NMR: δ = 8.13 (s, 3H), 3.87 (t, 3H), 3.1 (t, 2 H), 1.94 (m, 2H), 1.74 (m, 2H), 1.50 (m, 2H) ppm. ^{13}C-NMR: δ = 172.7, 55.8, 33.9, 24.7, 29.0, 42.6 [dark yellow solid at RT].

L-Arginine iodide (Arg–HI). ^{1}H-NMR: δ = 8.16 (s, 3H), 4.16 (t, 3H), 3.2 (t, 2 H), 1.55 (m, 2H), 1.78 (m, 2H) ppm. ^{13}C-NMR: δ = 173.7, 158.1, 55.7, 41.6, 28.5, 24.6 [dark brown viscous liquid at RT].

Coupling reaction

All the reactions were carried out in a 25 mL stainless-steel batch reactor with a magnetic stirrer at 800 rpm. In a typical batch reaction process, a pre-determined amount of the catalyst was charged into the reactor containing 35.5 mmol of SO. The reaction was carried out under a preset pressure of carbon dioxide at different temperatures. After the completion of the reaction, the reactor was cooled to RT and the products were identified by gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionized detector.

Reusability tests

After the reaction, 10 ml each of distilled water and dichloromethane was added to the reaction mixture. The organic layer and aqueous layer were separated using a separating funnel. The aqueous layer, upon concentrating using the rotary evaporator followed by drying under vacuum for 10 h at 60 °C, yielded the ionic liquids. Coupling reactions were performed again with the recovered ionic liquids as mentioned above.

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