Bifunctional Ionic Liquids Derived from Biorenewable Sources as Sustainable Catalysts for Fixation of Carbon Dioxide

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A series of highly efficient, bifunctional ionic liquids containing a quaternary alkyl ammonium cation and an amine anion were prepared from choline and amino acids, respectively. Nine ILs were synthesized, characterized, and applied as organocatalysts for the chemical fixation of carbon dioxide to form cyclic carbonates and quinazoline-2,4(1*H*,3*H*)-diones. A binary mixture of an IL and a co-catalysts generates deep eutectic solvents (DESs) and accelerates the rate of the cycloaddition reaction at atmospheric pressure and low temperature (70 °C). The

Introduction

The increased concentration of carbon dioxide in the atmosphere is an environmental threat and an important burning issue in our society. Carbon dioxide is kinetically and thermodynamically stable, but the utilization of carbon dioxide as a chemical feedstock provides interesting organic structures with high atom economy.^[1] Among these, carbonates are important as they can be used in various applications, including additives in fuel, aprotic solvents, monomers in polymeric structures, electrolytes in secondary batteries, and raw materials in various reactions.^[2] In the past decades, numerous catalytic systems have been developed for the catalytic fixation of carbon dioxide such as metal-salen complexes,^[3] metal oxides,^[4] N-heterocyclic carbenes,^[5] N-heterocyclic olefins,^[6] and Schiff bases.^[7] However, most of the catalytic systems suffer from one or more disadvantages such as low catalytic stability and reactivity, use of co-solvents, use of transition metals, harsh reaction conditions, catalyst degradation, and complicated methods for the synthesis of the catalysts.

lonic liquids (ILs) are a new emerging research area. The use of ILs for the fixation of carbon dioxide into value-added

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This publication is part of a Special Issue around the "1st Carbon Dioxide Conversion Catalysis" (CDCC-1) conference. A link to the issue's Table of Contents will appear here once it is complete. presence of the hydroxyl functional group of choline and the free amine group of the amino acids in the ILs has a synergistic effect on the activation of the epoxide and carbon dioxide towards the cycloaddition reactions. These ILs are biodegradable and are synthesized from easily available biorenewable sources. Additionally, this catalytic method demonstrates ultimate environmental benignity because of the mild metal- and solvent-free conditions as well as the recyclability of the catalyst and co-catalyst.

chemicals is considered cutting edge technology. ILs possess prominent features such as high thermal and chemical stability, non-flammability, low vapor pressure, easy recyclability, biodegradability, functional variability, and high solubility.^[8] The capture and fixation of carbon dioxide by using task-specific ILs is also a well-established area of research.^[9] Although various ILs have been synthesized and applied for carbon dioxide fixation, most of the processes for the synthesis of ILs require toxic reagents, and in some cases, the ILs are non-biodegradable.^[9b]

Chemical production that involves low value and readily available biomass feedstock with low environmental impact on the chemical processes helps to maintain the sustainability of the environment.^[10] Amino acids (AAs) and choline chloride (Ch) are both abundant and widely available in nature; therefore, ILs derived from these compounds are considered nontoxic and biodegradable.^[11] These types of ILs have also shown excellent activity for the dissolution of lignin and DNA.^[12] Additionally, the presence of a free amine group on the amino acids in ILs make them highly potent for the capture of carbon dioxide; therefore, they have been widely studied.^[13] Recently, Dai et al. reported that amino-acid-based ILs act as multimolar absorbing materials of carbon dioxide through the carboxylate group and the amine group.^[13g]

Catalysts bearing hydrogen bond donor (HBD) ability and amine functional groups are considered as highly active for the cycloaddition reaction of carbon dioxide with epoxides. The presence of a HBD activates the oxirane ring and promotes the cycloaddition reaction, whereas the existence of an amine group activates the carbon dioxide molecule. To date, various HBD catalysts such as silanols, phenols, glycerol, pentaerythritol, chitosan, lignin, cellulose, hydroxyl-functionalized imidazoles, urea-based ILs, pyridine alcohols, and covalent organic frameworks (COFs)^[14] have been developed for the syn-



thesis of cyclic carbonates. However, very few methods have been reported for the synthesis of carbonates under mild conditions (low temperature and low pressure).^[15] These methods suffer from some disadvantages such as multiple processes required for the syntheses of the catalysts, non-biodegradable catalysts, and activity for only one type of reaction. The fixation of carbon dioxide using organocatalysts is considered a cutting edge technology compared with other methods^[3c] owing to the robust, cheap, nontoxic, and air stable organic molecules, which do not necessarily need inert reaction conditions.^[15e] Although metal-containing catalysts show excellent activity towards carbon dioxide fixation, they are not considered as sustainable because non-biodegradable waste is generated during their use, which could contaminate the products.^[14]

The presence of a hydroxyl and an amine functional group (bifunctional) in [Ch][AA] IL encouraged us to use it for catalysis. Following our previous study towards the development of a catalytic system for the fixation of carbon dioxide,^[16] herein, we report the synthesis of environmentally benign, costeffective, and robust bifunctional ILs derived from choline and amino acids and their application for the catalytic fixation of carbon dioxide into cyclic carbonates and quinazoline-2,4(1H,3H)-diones. These synthesized ILs show high activity towards the fixation of CO₂ to form cyclic carbonates at atmospheric pressure. The catalyst and co-catalyst in the binary mixture are recyclable. This developed methodology is environmentally benign under solvent- and transition-metal-free conditions. Additionally, the synthesized ILs are nontoxic, recyclable, and biodegradable.

Results and Discussion

Nine ILs based on choline and amino acids were synthesized according to a method modified from the literature, as shown in Scheme 1.^[12] A simple and straightforward method was used for the synthesis of the ILs, in which the chlorine atoms of choline chloride were replaced by potassium hydroxide to afford choline hydroxide. Choline hydroxide reacted with the amino acids in a simple neutralization reaction to produce the ILs in excellent yield (>95%). This method for the synthesis of bifunctional ILs is environmentally friendly and more economical because of the safe byproducts, KCl and water, as well as the use of the cheap, easily available, and harmless choline and the amino acids as reactants. The synthesized ILs had a free amine group on the amino acid and a free hydroxyl group on the choline and could be used in catalytic reactions. The ILs were characterized by using various analytical techniques including nuclear magnetic resonance (NMR) spectroscopy (Supporting Information, Section S4) and FTIR (Figure 1). Because the stability of a catalyst is important to avoid the contamination of the product, the synthesized ILs were further characterized by using thermogravimetric analysis (TGA) (Figure 2). The ILs were found to be stable up to 200°C.

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Scheme 1. The synthesis of the ionic liquids (ILs) and their structures.



Figure 1. Comparative IR data of the synthesized [Ch][AA] ILs presence the functional group.

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2

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Figure 2. Thermogravimetric analysis (TGA) of the synthesized ILs showing the thermal stability of the [Ch][AA] IL up to 200 $^{\circ}$ C.

Catalytic performance of [Ch][AA] ILs for the synthesis of cyclic carbonates

To investigate the catalytic activity of the synthesized ILs, we investigated these ILs as catalysts for the synthesis of cyclic carbonates. Initially, the reaction of carbon dioxide with epichlorohydrin was used as the model reaction to study the various parameters at an atmospheric pressure of carbon dioxide (Table 1). The formation of cyclic carbonates was not observed without the use of ILs and co-catalysts (Table 1, entry 1–2).

Table 1. Catalyst screening for the synthesis of cyclic carbonates. ^[a]							
O [Ch][AA]/Co-cat							
	ci	4 + CO ₂	Solve	ent free CI	<u>`</u> `		
Entry	Catalyst	Co-cat.	T [°C]	Conversion [%] ^[b]	Selectivity [%] ^[b]		
1	-	-	25	-	-		
2	[Ch][Pro]	-	25	-	-		
3	[Ch][Pro]	TBAB	25	58	99		
4	[Ch][Pro]	TBAI	25	65	99		
5	[Ch][Pro]	KI	25	60	99		
6	[Ch][Pro]	TBAI	50	72	99		
7	[Ch][Pro]	TBAI	70	87	99		
8	[Ch][Gly]	TBAI	70	75	99		
9	[Ch][Val]	TBAI	70	73	99		
10	[Ch][Ala]	TBAI	70	77	99		
11	[Ch][Ser]	TBAI	70	81	99		
12	[Ch][Tyr]	TBAI	70	85	99		
13	[Ch][His]	TBAI	70	92	99		
14	[Ch][His]	TBAI	80	92	99		
15	[Ch][Try]	TBAI	70	90	99		
16	[Ch][4-OH-Pro]	TBAI	70	86	99		
17	-	TBAI	70	29	99		
18 ^[c]	[Ch][His]	TBAI	25	73	99		
19 ^[c]	[Ch][His]	TBAI	70	98	99		
20 ^[d]	[Ch][His]	TBAI	70	96	99		
21 ^[e]	[Ch][His]	TBAI	80	98	99		
[a] Reaction conditions: epichlorohydrin (20 mmol), IL/co-catalyst							
(20:20 mol%), 30 h, 1 atm CO_2 . [b] Determined by GC and GC–MS.							
[c] 1 MPa (CO ₂). [d] [Ch][His]/TBAI (10:10 mol%), 2 h, 1 MPa CO ₂ . [e–d] [Ch]							
[His]/TBAI (5:5 mol%), 2 h, 1 MPa CO ₂ .							

Next, we observed that the mixing of [Ch][Pro] IL with a quaternary ammonium salt such as tetrabutylammonium bromide (TBAB) generated deep eutectic solvents (DESs) with a low viscosity.^[12c] Surprisingly, with this binary mixture of IL and TBAB, a good yield of cyclic carbonates was observed at room temperature and atmospheric pressure of carbon dioxide (Table 1, entry 3). Co-catalysts such as tetrabutylammonium iodide (TBAI) and KI were also studied for the cycloaddition reaction. TBAI was found to be more active than KI (Table 1, entries 4-5). Increased yields of cyclic carbonates were obtained by increasing the temperature of the reaction system (Table 1, entries 6-7). The effect of various ILs on the cycloaddition reaction was investigated at 70 °C. Excellent yields of cyclic carbonate were observed using various ILs (Table 1, entries 8-16). Among them, [Ch][His] was found to be the most active and provided yields of cyclic carbonates of up to 92% owing to the presence and basic nature of the histidine (Table 1, entry 13). The high activity of [Ch][His] may be owing to the presence of another acidic proton on the imidazole ring, which could make it easier to open the epoxide ring. The increase in reaction temperature did not improve the yield of the carbonates (Table 1, entry 14). As a result, we concluded that $70 \,^\circ C$ was the optimal temperature for maximum conversion to the cyclic carbonates. The use of TBAI only provided a negligible amount of carbonate; hence, we decided that the ILs and TBAI show a synergistic effect on the activation of the epoxide as well as carbon dioxide (Table 1, entry 17). Next, we studied the effect of increasing the carbon dioxide pressure to 1 MPa on the cycloaddition reaction at room temperature. A good yield was obtained when [Ch][His] was used as the catalyst and TBAI was used as the co-catalyst (Table 1, entry 18). An excellent yield (up to 98%) of cyclic carbonates was obtained at 70°C (Table 1, entry 19). Next, we studied the effect of IL loading on the cycloaddition reaction. We found that at the atmospheric pressure of carbon dioxide and the catalyst loading play a critical role. A decreased carbonate yield was obtained with decreasing catalyst loading (Figure 3). The kinetic studies for the synthesis of cyclic carbonates were performed using the [Ch]



Figure 3. The effect of the [Ch][His] loading on the cycloaddition reaction; epichlorohydrin (20 mmol), [Ch][His]/TBAI, 30 h, 1 atm CO₂.

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Figure 4. The effect of reaction time on the conversion of oxirane to cyclic carbonate; [Ch][His]/TBAI (20:20 mol%), 1 atm CO_2.

[His] and TBAI catalyst mixture ([Ch][His]/TBAI). The results indicated that 30 h is required for maximum conversion to cyclic carbonate (Figure 4). Next, we studied the effect of time and catalyst loading at a slightly elevated temperature and at 1 MPa pressure of carbon dioxide. A decrease in the catalyst loading ([Ch][His]/TBAI 10:10 mol%) at 1 MPa pressure of carbon dioxide resulted in an excellent yield of up to 96% (Table 1, entry 20). A further decrease of the catalyst loading ([Ch][His]/TBAI 5:5 mol%) and a slight increase of the temperature to 80°C resulted in an excellent yield of up to 98% (Table 1, entry 21).

After optimization of the reaction conditions, we further extended this protocol for the study of different substrates for the formation of cyclic carbonates (Table 2). Various epoxides were reacted with carbon dioxide to yield cyclic carbonates under the optimized reaction conditions. [Ch][His] IL was used because of its higher reactivity for the formation of cyclic carbonates compared to the other ILs. Various aliphatic acyclic epoxides provided good yields of cyclic carbonates (Table 2, entries 1-3). In particular, the use of epichlorohydrin resulted in an excellent carbonate yield of up to 92%. Cyclic epoxides such as cyclopentyl oxide and cyclohexyl oxide also provided a good yield of cyclic carbonates (Table 2, entries 4-5). Next, we studied the aromatic epoxide styrene oxide, which showed good yields of styrene carbonate (Table 2, entry 6). Similarly, various aromatic epoxides functionalized with F, Cl, and Br substituents provided good yields of cyclic carbonates (Table 2, entries 6-9). Most importantly, the cyclic carbonates obtained using this protocol were obtained with high selectivity (>99%) and without any side products. The hydroxyl functional group in the ILs acts as a HBD catalyst and activates the epoxide ring, whereas the presence of the amine functional group of the amino acid activates the carbon dioxide molecules, resulting in a synergistic effect for the cycloaddition reaction.

We investigated the effect of different functional group on the cycloaddition reaction by using IR spectroscopy (Figure 5). Comparative IR data of the epoxide, ILs, and mixtures of both were taken at various intervals. After 2 h, a new peak appeared



at approximately 1781 cm⁻¹, which indicated the formation of a cyclic carbonate (Figure 5 d). A new peak appeared at approximately 1635.31 cm⁻¹ owing to the interaction between the carboxylate anion and the carbonate.^[13 g] The intensity of the carbonyl peak at approximately 1781 cm⁻¹ continued to increase up to 30 h (Figure 5 e to g). The effect of the HBD, which resulted in broadening of the peak resulting from the hydroxyl group, was also observed and discussed in the Supporting Information (Figure S1).

On the basis of previous reports and observed experimental data, we established a tentative mechanism for the cycloaddition reaction between carbon dioxide and an epoxide to cyclic carbonates catalyzed by ILs containing a HBD and an amine functional group (Figure 6).^[14] The coupling reaction between the carbon dioxide and the epoxide is initiated by the interaction between the hydroxyl group of the choline, which helps to polarize the C–O bond of the epoxide. Subsequently, the nucleophile of the co-catalyst attacks from the less hindered

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4



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Figure 5. IR spectroscopic study based on kinetic data (a) epichlorohydrin, (b) [Ch][His], (c) mixture of epichlorohydrin and [Ch][His] reaction mixture after (d) 2, (e) 4, (f) 12, and (g) 30 h and (h) the IR spectra of the carbonate after the reaction.



Figure 6. Proposed reaction mechanism for the synthesis of cyclic carbonate using [Ch][AA]/TBAI as a catalyst system.

side of the coordinated epoxide to open the ring. Then, the carbon dioxide molecule adsorbed by the amine group of the amino acid attacks the oxyanion of the epoxide to generate a carbonate anion, which subsequently undergoes ring closing to generate the cyclic carbonate. The effect of the HBD on the activation of the epoxide was investigated by using IR spectroscopy (Figure S1). Choline chloride was used as the reference HBD catalyst; the IR spectra of the epoxide, choline chloride, and a mixture of both were taken. The broadening of the peak attributed to the hydroxyl group of choline chloride and its shift from approximately 3232.12 to 3338.43 cm⁻¹ clearly indicates the presence of intermolecular hydrogen bonding between the epoxide and the choline chloride, which is responsible for the ring opening of the epoxide. The effect of the HBD catalysis was further explored by using NMR spectroscopy (Figure S2). After the addition of epoxide (epichlorohydrin) to a choline chloride solution (reference HBD catalyst in deuterated dimethylsulfoxide), the hydroxyl peak at 5.69 ppm completely disappears, which is clear evidence that hydrogen bonding of the catalyst plays a crucial role in the activation of the epoxide.



Figure 7. Recyclability of the ILs for the synthesis the cyclic carbonates. Reaction conditions: 1 atm CO_2 , epoxide (10 mmol), [Ch][His]/TBAI (10:10 mol%), 30 h; 1 MPa CO_2 , epoxide (10 mmol), [Ch][His]/TBAI (5:5 mol%), 2 h, 80 °C.

The recyclability of a catalysts is an important factor. We investigated the recyclability of the synthesized [Ch][AA] catalysts (Figure 7). [Ch][His] showed the highest activity towards the cycloaddition reaction of epichlorohydrin and CO_{2r} and was used as a model catalyst to investigate the recyclability. The recyclability tests were performed at atmospheric pressure and 1 MPa pressure of carbon dioxide. At atmospheric pressure the activity of the catalyst decreased slightly, which might be owing to the longer reaction time. At 1 MPa pressure of carbon dioxide the activity of the catalyst showed excellent yield after five cycles with negligible loss of activity.

After the successful application of ILs for the synthesis of cyclic carbonates, we extended this methodology for the synquinazoline-2,4(1*H*,3*H*)-diones. thesis of Ouinazoline-2,4(1H,3H)-diones are very important intermediates in the field of pharmaceuticals.^[17] The synthesis of quinazoline-2,4(1H,3H)dione from 2-aminobenzonitrile and carbon dioxide is considered an important pathway because of the direct utilization of carbon dioxide as well as the high atom economy. Although various methods have been reported for this transformation, they require high pressure, high temperature, or the use of non-biodegradable transition metals or toxic catalysts, which may contaminate the product.^[18] Hence, there is an immediate need to develop a catalytic system that is environmentally friendly and operates under mild reaction conditions.

As synthesized [Ch][AA] ILs were utilized for the synthesis of quinazoline-2,4(1H,3H)-dione (**2**) from 2-aminobenzonitrile (**1**) and carbon dioxide (2 MPa) at 100 °C (Table 3). No quinazoline-2,4(1H,3H)-dione was obtained without the use of ILs (Table 3, entry 1). [Ch][Gly] provided a good yield of **2.** Further, we screened various [Ch][AA] ILs (Table 3, entries 2–10) for the synthesis of quinazoline-2,4(1H,3H)-dione and found that the ILs containing proline, tryptophan, and histidine were highly reactive. Among the screened ILs, it was found that [Ch][His] has excellent activity and provides yields of up to 83% (Table 3, entry 7). The developed methodology was also utilized to investigate the use of different substrates for the synthesis of



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other quinazoline-2,4(1 H,3 H)-diones. 2-aminobenzonitrilebased substrates containing methyl, chloro, and nitro functional group were reacted with carbon dioxide to afford the corresponding quinazoline-2,4(1 H,3 H)-diones in good yields (Table 3, entries 11–13). The acid–base nature of the ILs effectively activates the 2-aminobenzonitrile and carbon dioxide and provides good yields of the quinazoline-2,4(1 H,3 H)-diones

Conclusions

A simple, sustainable, cost-effective, and energy-efficient protocol has been developed for the chemical fixation of carbon dioxide into cyclic carbonates as well as quinazoline-2,4(1H,3H)diones using choline- and amino-acid-based ionic liquids (ILs). The binary system based on [Ch][AA]/TBAI generated deep eutectic solvents (DESs), which were found to be highly active for the catalysis of the cycloaddition of carbon dioxide with epoxides at atmospheric pressure. These catalysts can effectively activate epoxides through a synergistic effect of a hydroxyl group at the choline cation and carbon dioxide at the amine anion of the amino acids. The catalyst and the co-catalyst are both recyclable up to five cycles without loss of catalytic activity. Additionally, the ILs were synthesized from environmentally friendly starting materials that are highly biodegradable and have negligible toxicity, which is a promising for the fixation of carbon dioxide.

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7

FULL PAPERS

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 Bifunctional Ionic Liquids Derived
 from Biorenewable Sources as
 Sustainable Catalysts for Fixation of Carbon Dioxide



Bifunctional Catalysts! Ionic liquids containing a quaternary alkyl ammonium cation and an amine anion are prepared and applied as organocatalysts for the chemical fixation of carbon dioxide to form cyclic carbonates and quinazoline-2,4(1 *H*,3 *H*)-diones. The presence of a hydroxyl group and a free amine group in the ILs has a synergistic effect on the activation of epoxides and carbon dioxide and the subsequent cycloaddition reactions.