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Novel functionalized guanidinium ionic liquids: Efficient acid–base bifunctional catalysts for CO_2 fixation with epoxides

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ABSTRACT

A series of functional guanidinium-based ionic liquids (FGBILs) that contain both Lewis acid and basic sites was prepared by a simple method, and used as catalysts for the synthesis of cyclic carbonates through the cycloaddition of CO_2 to epoxides in the absence of co-catalyst and solvent. Propylene oxide conversion was near completion at 130 °C and 2.5 MPa in 2 h when $[TMGC_2H_4NH_2]Br$ was used as catalyst. The effects of functional groups and counter anions on catalytic performance were investigated. The synergistic effect of polarization by hydrogen bonding and the nucleophilic attack by bromide anion account for the facile ring-opening of epoxide. Furthermore, the protocol is applicable to a variety of terminal epoxides, producing the corresponding cyclic carbonates in high yield and selectivity. It is envisaged that the metal- and solvent-free process using a single catalyst has high potential for large-scale fixation of CO_2.

1. Introduction

Carbon dioxide is a renewable C1 resource that is abundant, inexpensive and nontoxic. The fixation of CO_2 for the generation of useful compounds has attracted much attention [1]. There are over 20 known chemical reactions that involve CO_2 as starting material, but CO_2 fixation in an industrial scale remains as a challenge [2]. One of the promising processes is the cycloaddition of CO_2 to epoxides for the formation of cyclic carbonates. Cyclic carbonates are valuable compounds that are used as polar solvents, electrolytes in lithium secondary batteries, precursors for synthesizing polycarbonates and polyurethanes, and intermediates for production of pharmaceuticals, fine chemicals, and agricultural chemicals [1–4].

With an atom utilization ratio of 100%, the cycloaddition of CO_2 to epoxides is in accord with the concept of "green chemistry" and "atom economy" [5]. In the past decades, numerous catalysts have been developed for the synthesis of cyclic carbonates. In recent years, ionic liquids (ILs) have received more attention than the other catalysts (such as alkali metal salts [6], metal oxide [7–9], modified molecular sieve [10,11], and organometallic complexes [12–15]) because they are low-cost, good in solvating ability as well as being variable in polarity and adjustable in structure and acid–base properties. So far, imidazolium salts [16–23], quaternary ammonium salts [22,24,25], quaternary phosphonium salts [26,27], pyridinium salts [28], and gunidinium salts [29–31], and other ILs [32,33] have been reported as efficient catalysts for CO_2 fixation through the synthesis of cyclic carbonates from epoxides. Although the advances are significant, most of the ILs showed shortcomings such as unsatisfactory activity, harsh reaction conditions, being water and/or air sensitive, and the need of a metal salt as co-catalyst. From the viewpoints of industrial production and environment friendliness, it is highly desirable to develop a stable single-component catalyst that functions well under mild reaction conditions.

There is increasing investigation on guanidinium ILs because they are thermally as well chemically stability. With tunable groups on the N atoms, they show excellent catalytic activity for organic reactions [34]. Compared to the use of imidazolium-based ILs for the cycloaddition of CO_2 to epoxides, the use of guanidinium-based ILs (GBILs) is rare. Xie et al. [29] reported that hexabutylguanidinium chloride showed certain activity for the cycloaddition reaction, but the reaction time was long and large amount of catalyst was needed. Later on, the researchers reported the observation of high activity over a hexabutylguanidinium bromide/$ZnBr_2$ binary system, but $ZnBr_2$ is required as a co-catalyst [30]. Furthermore, Dou et al. [31] synthesized PEG that was functionalized with guanidinium salt which showed certain activity for cycloaddition reaction. Recently Sun et al. reported that hydroxyl- and

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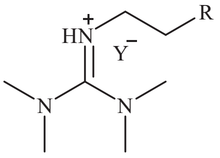

1a: R = NH_2, Y = Br; **1b**: R = COOH, Y = Br; **1c**: R = OH, Y = Br; **1d**: R = CH_3, Y = Br; **1e**: R = H, Y = Br

2a: R = NH_2, Y = BF_4;
3a: R = NH_2, Y = PF_6

Scheme 1. Structures of FGBILs.

carboxyl-functionalized imidazolium-based ILs showed good catalytic activity for cycloaddition reactions [22,23]. As far as we know, there is no report on the synthesis of functionalized guanidinium-based ILs (FGBILs) and their use as catalysts for the synthesis of cyclic carbonate.

In the present work, a series of FGBILs (Scheme 1) were synthesized, and for the first time used as catalysts for the cycloaddition of CO_2 to epoxides in the absence of solvent and co-catalyst. We studied in detail the roles of functional group attached to the cation as well as the role of the counter anion. Furthermore, a systematic investigation was conducted on the effects of reaction parameters (catalyst loading, temperature, time and initial CO_2 pressure) on the catalytic reaction.

2. Experimental

2.1. Chemicals

The tetramethylguanidine, 2-bromoethanol, 3-bromopropionic acid, bromoethane, 1-bromopropane, $NaBF_4$, and KPF_6 were purchased from Shanghai Jingchun Industry Co., Ltd. 2-Bromoethylamine hydrobromide was purchased from Aldrich Chemical Co. Propylene oxide and ethylene oxide were produced by Sinopharm Chemical Reagent Co., Ltd. The other epoxides were purchased from Alfa Aesar China Co., Ltd. All chemicals were used as received. The CO_2 (99.9% purity) purchased from Nanchang Guoteng Gas Co. was used without any further treatment.

2.2. Characterization

The products were analyzed on a gas chromatograph (Agilent 7890A) that was equipped with a FID and a DB-wax capillary column (30 m × 0.53 mm × 1.0 μm). NMR spectra were recorded on a Bruker 400 spectrometer in DMSO-d_6. ^1H NMR chemical shifts (δ) in ppm were downfield from tetramethylsilane. Elemental analysis was performed over a Vario EL III analyzer. The FT-IR spectra were recorded using a Bruker vertex 70 FT-IR spectrophotometer. All reagents were used as received.

2.3. Preparation and characterization of guanidinium-based ILs

A typical procedure for preparation of $[TMGC_2H_4NH_2]Br$ (**1a**) is as follows: a solution of tetramethylguanidine (TMG) (40 mmol) in MeCN (12 mL) was prepared at 0 °C under N_2 atmosphere in a dry round-bottomed flask equipped with a reflux condenser. Another solution of 2-bromoethylamine hydrobromide (40 mmol) in MeCN (6 mL) was added dropwise to the flask, and the mixture was heated to room temperature and stirred for 24 h. Afterward, the solvent was removed, and the resulted solid was washed three times with triethylamine and ethyl acetate respectively, then dried at 60 °C under vacuum for 12 h to give product **1a** as a white solid. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.84$ (s, 1H), 3.14–3.08 (m, 2H), 2.92 (s, 12H), 1.23 (t, $J = 7.2$ Hz, 2H); Anal. calcd for $C_7H_{19}N_4Br$: C 35.15, H 8.01, N 23.43, found: C 35.27, H 8.08, N 23.55.

Other guanidinium ILs (**1b–e**) were prepared following the same method but without the procedure of washing with triethylamine. $[TMGC_2H_4COOH]Br$ (**1b**): white solid; ^1H NMR (400 MHz, DMSO-d_6): ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.80$ (s, 1H), 3.28 (s, 4H), 2.90 (s, 12H); anal. calcd for $C_8H_{18}N_3O_2Br$: C 35.83, H 6.77, N 15.67, found: C 35.72, H 6.72, N 15.51; $[TMGC_2H_4OH]Br$ (**1c**): white solid; ^1H NMR (400 MHz, DMSO-d_6): ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.80$ (s, 1H), 3.30 (s, 4H), 2.90 (s, 12H); Anal. calcd for $C_7H_{18}N_3OBr$: C 35.01, H 7.56, N 17.50, found: C 34.96, H 7.50, N 17.64; $[TMGC_2H_4CH_3]Br$ (**1d**): colorless liquid; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.81$ (s, 1H), 3.16–3.08 (m, 2H), 2.92 (s, 12H), 1.61–1.52 (m, 2H), 0.90–0.70 (m, 3H); Anal. calcd for $C_8H_{20}N_3Br$: C 40.34, H 8.46, N 17.64, found: C 40.48, H 8.56, N 17.75; $[TMGC_2H_5]Br$ (**1e**): colorless liquid; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.76$ (s, 1H), 3.27–3.15 (m, 2H), 2.92 (s, 12H), 1.13 (dt, $J = 7.2$ Hz, 3H); anal. calcd for $C_7H_{18}N_3Br$: C 37.51, H 8.09, N 18.75, found: C 37.78, H 7.92, N 18.91.

The ionic liquid **2a** and **3a** were synthesized by anion exchange between ionic liquid **1a** and the corresponding inorganic salt. A typical synthesis route to $[TMGC_2H_4NH_2]BF_4$ (**2a**) is as follows: solid $NaBF_4$ (2 mmol) was added to a solution of **1a** (2 mmol) in H_2O (10 mL), and the mixture was stirred vigorously at room temperature for 10 h. The solution was extracted with CH_2Cl_2 (3 × 10 mL), and the organic phase was collected and dried with anhydrous Na_2SO_4 for 24 h. The organic solution was subject to evaporation for solvent removal, and the resulted product was dried at 60 °C under vacuum for 12 h to give product **2a** as a white solid. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.77$ (s, 1H), 3.13–3.07 (m, 2H), 2.90 (s, 12H), 1.20 (t, $J = 7.0$ Hz, 2H); anal. calcd for $C_7H_{19}N_4BF_4$: C 34.17, H 7.78, N 22.77, found: C 34.35, H 7.72, N 22.94.

The ionic liquid $[TMGC_2H_4NH_2]PF_6$ (**3a**) was prepared by the same method but using KPF_6 rather than $NaBF_4$. $[TMGC_2H_4NH_2]PF_6$ (**3a**): white solid; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.76$ (s, 1H), 3.13–3.07 (m, 2H), 2.90 (s, 12H), 1.19 (t, $J = 7.2$ Hz, 2H); anal. calcd for $C_7H_{19}N_4PF_6$: C 27.64, H 6.30, N 18.42, found: C 27.92, H 6.41, N 18.57.

The imidazolium IL (1-(2-hdyroxyl-ethyl)-3-methyl-imidazolium, $[MImC_2H_4OH]Br$) and quaternary ammonium IL (hydroxyl-ethyl-triethylammonium bromide, $[TEAC_2H_4OH]Br$) were prepared according to the procedures reported in Ref. [22]. $[MImC_2H_4OH]Br$: white solid; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 9.24$ (s 1H), 7.79 (d, 2H), 5.17 (s, 1H), 4.26 (t, $J = 8.2$ Hz, 2H), 3.89

Table 1
Performance of various catalysts.[a]

Entry	Catalyst	Catalytic results	
		Yield (%)	Sel. (%)
1	TMG	1.8	88.5
2	$[TMGC_2H_4NH_2]Br$ (**1a**)	94.6	99.8
3	$[TMGC_2H_4COOH]Br$ (**1b**)	90.8	99.9
4	$[TMGC_2H_4OH]Br$ (**1c**)	88.3	99.8
5	$[TMGC_2H_4CH_3]Br$ (**1d**)	71.6	99.8
6	$[TMGC_2H_5]Br$ (**1e**)	62.8	99.7
7	$[TMGC_2H_5]Br/CH_3(CH_2)_2NH_2$[b]	80.3	99.6
8	$[TMGC_2H_5]Br/CH_3COOH$[b]	78.0	99.7
9	$[TMGC_2H_5]Br/CH_3CH_2OH$[b]	78.8	99.7
10	$CH_3CH_2CH_2NH_2$	6.0	99.0
11	CH_3COOH	1.6	98.6
12	CH_3CH_2OH	1.9	99.1
13	$[TMGC_2H_4NH_2]BF_4$ (**2a**)	3.1	99.1
14	$[TMGC_2H_4NH_2]PF_6$ (**3a**)	2.7	99.0
15	$[MImC_2H_4OH]Br$[c]	58.1	99.6
16	$[TEAC_2H_4OH]Br$[c]	49.6	99.6
17	KBr	3.4	99.3
18	TMG/KBr [b]	48.5	99.0

[a] Reaction conditions: PO 35.7 mmol, cat. 0.5 mol%, initial CO_2 pressure 2.0 MPa, temp. 130 °C, time 2 h.

[b] Equal catalyst amount (0.179 mmol).

[c] $[MImC_2H_4OH]Br$ (1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide) and $[TEAC_2H_4OH]Br$ (2-hydroxyl-ethyl-triethylammonium bromide) were prepared according to Ref. [22].