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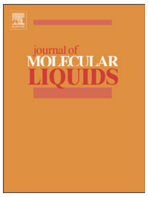

Synergistic cooperation of bi-active hydrogen atoms in protic carboxyl imidazolium ionic liquids to push cycloaddition of CO_2 under benign conditions

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ABSTRACT

Nine protic carboxyl imidazolium ionic liquids are synthesized. Then, they are employed to catalyze the chemical fixation of carbon dioxide (CO_2) and propylene oxide leading to propylene carbonate in the absence of co-catalyst and organic solvent. HCPImBr presents the best catalytic activity with the product yield of 92% under reaction temperature 120 °C, CO_2 initial pressure 1.5 MPa, catalyst amount 0.5 mol%, and reaction time 2.0 h. Even if the reaction temperature and CO_2 initial pressure are decreased to 80 °C and 1.0 MPa, respectively, the 85% of product yield would be kept with the 1.0% catalyst dosage along with 12.0 h. With the exception of the most optimal reaction conditions, generality, and recyclability of HCPImBr are also investigated. More importantly, the reaction mechanism is investigated by the density functional theory, which is the first time to report the mechanism for protic carboxyl imidazolium ionic liquids. The catalytic activity of ionic liquids would be further improved with the reasonable combination of cation and anion.

1. Introduction

As a plentiful safe, and cheap C1 resources, the utilization of carbon dioxide (CO_2) to produce the useful organic chemicals has attracted much attention [1]. It is not only beneficial to ameliorating the greenhouse effect but also helpful to solve the depletion of fossil fuels [2]. One of the most successful reactions is the coupling reaction of CO_2 to epoxides resulting in cyclic carbonate [3–5] (See Scheme 1) because of the advantages of atom-efficiency and low-cost. Moreover, the cyclic carbonate is widely applied as industrial raw materials [6], electrolytes in lithium-ion secondary batteries [7], polar aprotic solvents [8], precursors for polycarbonates [9], and pharmaceutical intermediates [10].

In past two decades, some catalysts have been reported for the synthesis of cyclic carbonate [11,12]. Ionic liquids (ILs) stands out from them because of their negligible volatility, environmental benign, easy separation, and others [13,14]. However, traditional ILs [15,16] are rarely taken as single-component catalyst because of the low catalytic reactivity and requirement of solvent and metal. The incorporation of co-catalyst is a facile approach to effectively improve the catalytic activity [17,18]. The addition of Lewis acids [19] is a typical choice. However, most of Lewis acids are sensitive to the water resulting in the more complex synthesis operation and higher production cost. An alternative method is to involve a suitable amount of solvent containing hydroxyl group [20].

Inspired by it, the hydroxyl functionalized imidazolium ILs are reported by Sun et al. [21]. They present the better catalytic activity than the corresponding imidazolium ILs without hydroxyl group for the coupling reaction. Later, hydroxyl functionalized quaternary ammonium [22], hydroxyl functionalized isothiouronium [23], and hydroxyl functionalized guanidinium [24] ILs are developed in succession with the similar performance. The theoretical studies have uncovered that the hydrogen bond between hydrogen bond donor and oxygen atom of propylene oxide (PO) would greatly promote the ring-opening of PO [25,26]. As the stronger hydrogen bond donor, involvement of carboxyl

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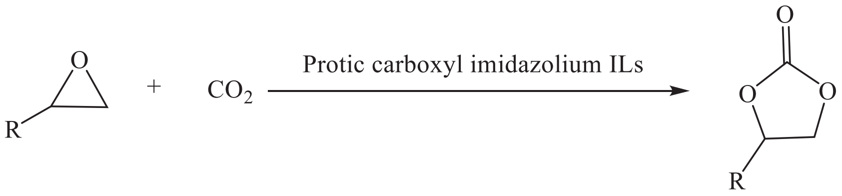


Scheme 1. Cycloaddition reaction of CO_2 and epoxides catalyzed by protic carboxyl imidazolium ILs.

group would lead to the higher catalytic activity. Later, the carboxyl functionalized imidazolium ILs have been developed [27,28] to testify the aforementioned viewpoint.

The other important subgroup of ILs is protic ILs that are formed by equimolar amounts of Brønsted acid and base with unique properties including low cost and easy preparation [29]. In protic ILs, there would be proton-donor and proton-acceptor sites induced by the proton transfer from the acid to the base, which is beneficial to building the hydrogen bond. Some protic quaternary ammonium ILs have been developed by Liu et al. [30]. To catalyze the fixation of CO_2. Both the protic ILs and task functionalized ILs have the better catalytic activity than the corresponding traditional ILs.

Perhaps protic carboxyl imidazolium ILs are expected to have the better catalytic performance than both protic ILs and carboxyl functionalized ILs. To our best knowledge, they have never been reported. In this work, nine protic carboxyl imidazolium ILs (See Scheme 2) are synthesized by a simple two-step reaction. They would catalyze the coupling reaction of CO_2 and PO without any metal and solvent [31,32]. The influence of ionic liquids on the catalytic performance is investigated including the functionalized group, chain length in cation, and different anions. Moreover, the optimal reaction conditions are determined. The generality, thermal stability, and reusability of protic carboxyl imidazolium ILs are also considered. Finally, the reaction mechanism is explored by density functional theory (DFT) to uncover the mechanism from atomic level. It is expected that an efficient IL with excellent catalytic activity would be developed for the fixation of CO_2 by the simple synthesized step under mild condition.

2. Experiment

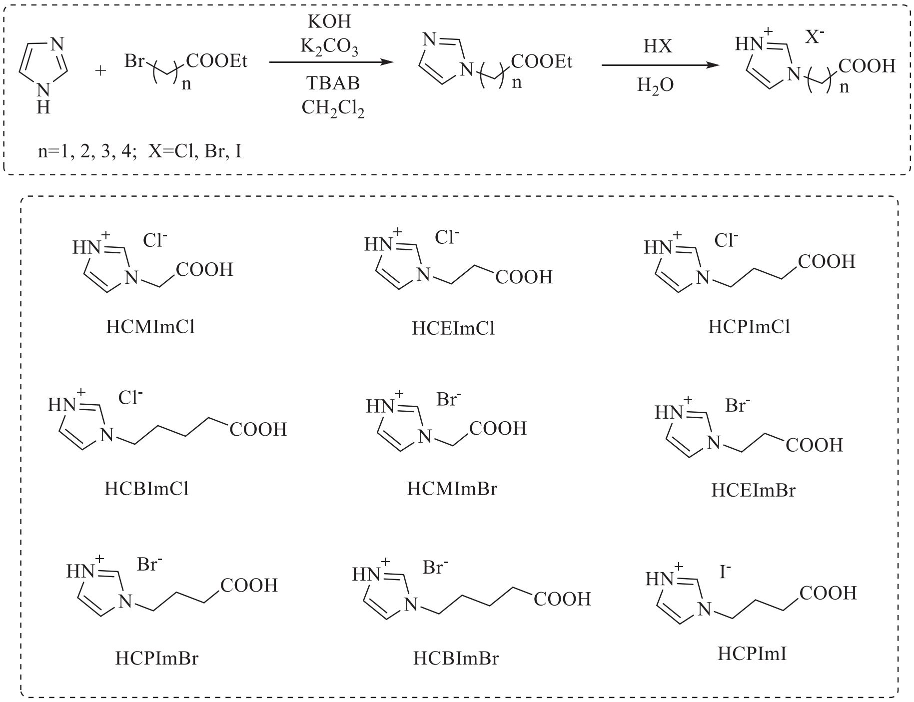
2.1. Instruments and materials

The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were run on Bruker AVANCE III HD spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded with Agilent 1100LC-MS mass spectrometer. The thermal decomposition temperature was analyzed with thermal gravimetric analyzer (Mettler Toledo TGA/SDTA851e). Elemental analyses (EA) were measured with Vario EL cube elemental analyzer. Single-crystal X-ray diffraction (XRD) measurement was carried out on a Bruker CCD Apex II X-ray single-crystal diffractometer. GC analyses were performed on Agilent GC–7890 B using a flame ionization detector.

The imidazole and halogen esters were purchased from Shanghai Dibo Biotechnology Co. Ltd.. PO was produced by Sinopharm Chemical Reagent Co. Ltd. Other epoxides were purchased from Shanghai Macklin Biochemical Co. Ltd.. The CO_2 (99.9%) was purchased from Xinri Gas Co. Ltd.. All of the reagents and solvents were used without further purification.

2.2. Preparation and characterization of protic carboxyl imidazolium ILs

These protic carboxyl imidazolium ILs were prepared by two steps including synthesis of carboxylic ester substituted imidazole [33] and formation of protic carboxyl imidazolium ILs including hydrolytic process and protonation process [34] (See Scheme 2). For example, 1-



Scheme 2. Synthesis route and structures of protic carboxyl imidazolium ILs.

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carboxymethyl imidazolium bromide was prepared by the following method:

Imidazole (6.8 g, 0.1 mol) was dissolved in CH_2Cl_2 (75 ml). Then, KOH (8.4 g, 0.15 mol), K_2CO_3 (13.8 g, 0.1 mol), and tetrabutyl ammonium bromide (TBAB) (0.7 g, 0.002 mol) were added and stirred at room temperature for 30 min. Subsequently, the solution was treated dropwise with ethyl 2-bromoacetate (16.7 g, 0.1 mol) for about 30 min, and the mixture was heated to reflux for 7.0 h. The resulting precipitate was filtered and washed with CH_2Cl_2 (40 × 3 ml). Then, the filtrate was washed with saturated NaCl solution, and the aqueous layer was separated. The organic layer was evaporated to obtain the wine red liquid 1-ethoxycarbonyl methyl imidazole, which was used without any further purification for the next step.

Hydrochloric acid (5.92 g, 60 mmol) was added dropwise to 1-ethoxycarbonyl methyl imidazole (4.62 g, 30 mmol), and the mixtures were stirred for 15.0 h at room temperature (25 °C) to ensure that all of the substrate were reacted. Ethanol was separated by rotary evaporation. Then water was removed by using cyclohexane as water-carrying agent. Under the heating condition. Finally, the residue was washed repeatedly with ethyl acetate in reflux condition and dried in vacuum to obtain 1-carboxymethyl imidazolium chloride (HCMImCl).

Other protic carboxyl imidazolium ILs were prepared with a similar procedure to HCMImCl. The structures of protic carboxyl imidazolium ILs were characterized by NMR, MS (ESI), and EA. Particularly, HCMImBr was also characterized by XRD, and the result of crystal test further confirmed the correctness of structure of HCMImBr. The single crystal specimen of HCMImBr was acquired via slow evaporation of their solutions (V_{MeOH}:V_{CHCl3}≈1:5, the sample was dissolved by a small amount of methanol, and then chloroform was added) at room temperature, and the crystallographic data of HCMImBr is listed in Table S1. Furthermore, ^1H and ^{13}C NMR spectra are showed in Fig. S1, other data was provided as follows:

1-carboxymethyl imidazolium chloride (HCMImCl): Light yellow solid (Yield: 76.51%). ^1H NMR (400 MHz, D_2O) δ 8.79 (s, –CH–, 1H), 7.51 (m, –CH=CH-, 2H), 5.12 (s, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 169.73, 135.83, 122.99, 119.45, 49.66. MS (ESI): $[C_5H_7N_2O_2]^+$ m/z 127.25. Anal. Calcd for $C_5H_7N_2O_2Cl$: C, 36.94, N, 17.23, H, 4.34. found: C,36.60, N, 17.45, H, 4.068.

1-carboxyethyl imidazolium chloride (HCEImCl): Light yellow solid (Yield: 73.45%). ^1H NMR (400 MHz, D_2O) δ 8.77 (s, –CH–, 1H), 7.54 (d, J = 2.7 Hz, –CH–, 1H), 7.44 (d, –CH–, 1H), 4.52 (t, J = 6.3 Hz, –CH_2-, 2H), 3.00 (t, J = 7.4 Hz, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 174.10, 134.98, 121.83, 119.65, 44.67, 33.98. MS (ESI): $[C_6H_9N_2O_2]^+$ m/z 141.22.

1-carboxypropyl imidazolium chloride (HCPImCl): Light yellow solid (Yield: 80.83%). ^1H NMR (400 MHz, D_2O) δ 8.76 (s, –CH–, 1H), 7.54 (d, –CH–, 1H), 7.47 (d, –CH–, 1H), 4.31 (t, J = 7.1 Hz, –CH_2-, 2H), 2.45 (t, J = 7.2 Hz, –CH_2-, 2H), 2.20 (m, J = 7.2 Hz, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 176.67, 134.52, 121.81, 119.81, 48.38, 30.31, 24.75. MS (ESI): $[C_7H_{11}N_2O_2]^+$ m/z 155.20. Anal. Calcd for $C_7H_{11}N_2O_2Cl$: C, 44.11, N, 14.70, H, 5.82. found: C, 44.39, N, 14.38, H, 5.161.

1-carboxybutyl imidazolium chloride (HCBImCl): White solid (Yield: 78.59%). ^1H NMR (400 MHz, D_2O) δ 8.76 (s, –CH–, 1H), 7.54 (s, –CH–, 1H), 7.49 (s, –CH–, 1H), 4.29 (t, J = 7.1 Hz, –CH_2-, 2H), 2.44 (t, J = 7.3 Hz, –CH_2-, 2H), 1.96 (m, J = 7.3 Hz, –CH_2-, 3H), 1.62 (m, J = 7.4 Hz, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 177.98, 134.33, 121.73, 119.70, 48.94, 32.95, 28.62, 20.89. MS (ESI): $[C_8H_{13}N_2O_2]^+$ m/z 169.07. Anal. Calcd for $C_8H_{13}N_2O_2Cl$: C, 46.95, N, 13.69, H, 6.40. found: C, 46.76, N, 13.55, H, 6.416.

1-carboxymethyl imidazolium bromide (HCMImBr): Gray solid (Yield: 83.16%). ^1H NMR (400 MHz, D_2O) δ 8.45 (s, J = 1.5 Hz, –CH–, 1H), 7.16 (dt, J = 9.3, 1.9 Hz, –CH=CH-, 2H), 4.42 (s, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 169.83, 135.89, 123.06, 119.51, 49.82. MS (ESI): $[C_5H_7N_2O_2]^+$ m/z 127.25. Anal. Calcd for $C_5H_7N_2O_2Br$: C, 29.01, N, 13.53, H, 3.41. found: C, 29.47, N, 13.68, H, 3.354.

1-carboxyethyl imidazolium bromide (HCEImBr): Light yellow solid (Yield: 62.43%). ^1H NMR (400 MHz, D_2O) δ 8.82 (s, –CH–, 1H), 7.58 (d, J = 1.7 Hz, –CH–, 1H), 7.49 (d, J = 1.7 Hz, –CH–, 1H), 4.56 (t, J = 6.3 Hz, –CH_2-, 2H), 3.05 (t, J = 6.3 Hz, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 174.08, 135.02, 121.90, 119.69, 44.73, 34.05. MS (ESI): $[C_6H_9N_2O_2]^+$ m/z 141.20. Anal. Calcd for $C_6H_9N_2O_2Br$: C, 32.60, N, 12.67, H, 4.10. found: C, 32.89, N, 12.86, H, 4.213.

1-carboxypropyl imidazolium bromide (HCPImBr): White solid (Yield: 74.33%). ^1H NMR (400 MHz, D_2O) δ 8.69 (s, –CH–, 1H), 7.46 (d, J = 1.7 Hz, –CH–, 1H), 7.40 (d, J = 1.7 Hz, –CH–, 1H), 4.24 (t, J = 7.1 Hz, –CH_2-, 2H), 2.38 (t, J = 7.2 Hz, –CH_2-, 2H), 2.13 (m, J = 7.2 Hz, –CH2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 176.75, 134.55, 121.84, 119.83, 48.42, 30.34, 24.77. MS (ESI): $[C_7H_{11}N_2O_2]^+$ m/z 155.20. Anal. Calcd for $C_7H_{11}N_2O_2Br$: C, 35.77, N, 11.92, H, 4.72. found: C, 36.30, N, 11.77, H, 5.012.

1-carboxybutyl imidazolium bromide (HCBImBr): Light yellow solid (Yield: 78.17%). ^1H NMR (400 MHz, D_2O) δ 8.78 (s, J = 1.5 Hz, –CH–, 1H), 7.56 (d, J = 1.8 Hz, –CH–, 1H), 7.51 (d, J = 1.7 Hz, –CH–, 1H), 4.31 (t, J = 7.1 Hz, –CH_2-, 2H), 2.47 (t, J = 7.3 Hz, –CH_2-, 2H), 1.97 (m, –CH_2-, 2H), 1.64 (m, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 177.90, 134.36, 121.78, 119.73, 48.99, 33.00, 28.66, 20.92. MS (ESI): $[C_8H_{13}N_2O_2]^+$ m/z 169.07. Anal. Calcd for $C_8H_{13}N_2O_2Br$: C, 38.57, N, 11.25, H, 5.26. found: C, 38.95, N, 11.01, H, 5.510.

1-carboxypropyl imidazolium iodide (HCPImI): Yellow green solid (Yield: 83.13%). ^1H NMR (400 MHz, D_2O) δ 8.78 (s, –CH–, 1H), 7.55 (d, –CH–, 1H), 7.49 (d, –CH–, 1H), 4.33 (t, J = 7.1 Hz, –CH_2-, 2H), 2.46 (t, J = 7.2 Hz, –CH_2-, 2H), 2.22 (m, J = 7.2 Hz, –CH_2-, 2H). ^{13}C NMR (101 MHz, D_2O) δ 176.87, 134.53, 121.81, 119.79, 48.40, 30.33, 24.73. MS (ESI): $[C_7H_{11}N_2O_2]^+$ m/z 155.20. Anal. Calcd for $C_8H_{13}N_2O_2I$: C, 29.81, N, 9.93, H, 3.93. found: C, 29.83, N, 9.30, H, 3.684.

2.3. Cycloaddition reaction of CO_2 and epoxides

The cycloaddition reaction of CO_2 and epoxides catalyzed by protic carboxyl imidazolium ILs was carried out in 100 ml high-pressure reaction autoclave equipped with a magnetic stirrer. For a typical reaction process: Protic carboxyl imidazolium IL (0.50 mmol) and propylene oxide (100 mmol) were added into the reactor vessel without any co-solvent and co-catalyst. CO_2 was charged into the reactor to a certain pressure (0.5–3.0 MPa). Then the reactor was stirred and heated at 90–130 °C for 0.5–2.5 h. After the reaction, the reactor was cooled to room temperature and the remaining CO_2 was slowly released. Finally, the products were obtained by separation. In order to verify the yield and selectivity, the products were detected by GC analysis. According to the aforementioned data, the purity of synthesized ionic liquids is near to 100%. The influence of impurities is negligible.

3. Results and discussion

3.1. Synthesis and stability of ILs

Nine protic carboxyl imidazolium ILs have been synthesized by a simple two-step reaction, alkylation reaction to synthesize 1-ethoxycarbonyl imidazole and protonation reaction to produce protic carboxyl imidazolium ILs (See Scheme 2). In the first step, only the 1-ethoxycarbonyl imidazole is got, which is not hydrolyzed to 1-carboxyl imidazole. Then, hydrolysis reaction and protonation reaction are simultaneously completed in the present of two equivalent corresponding halogenated acid at room temperature resulting in protic carboxyl imidazolium ILs. The simplified reaction steps would greatly reduce the synthetic cost and time. Finally, the structures of desired products are confirmed by the NMR, MS, and EA.

The thermal stability of four protic carboxyl imidazolium ILs, HCMImBr, HCEImBr, HCPImBr, and HCBImBr are studied by thermogravimetric analysis (TGA) as representative (See Fig. S2). There is a one-stage decomposition in the TGA curves with the first turning point above 240 °C. According to previous literature, the reaction temperature is not higher than 140 °C for coupling reaction of CO_2 and PO catalyzed by ILs [35]. Therefore, the protic carboxyl imidazolium ILs would not decompose in the following catalytic process. The decomposed temperatures are 281.3 °C for HCMImBr, 246.4 °C for HCEImBr, 283.0 °C for HCPImBr, and 291.1 °C for HCBImBr with 10% weight loss.

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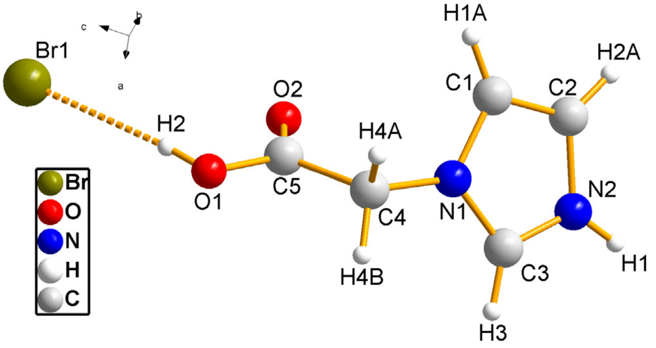

Fig. 1. The crystal structure of HCMImBr.

3.2. Single crystal X-ray crystallography

The crystal structure of HCMImBr is shown in Fig. 1. The crystallographic data of HCMImBr is listed in Table S2 along with the measured bond lengths and angles. The bond lengths involved in the imidazole ring, including C═C, C–N, and C═N bonds, are neither typical double bond nor single bond suggesting the conjugation of the imidazole rings. The C3–N1 and C3–N2 bond lengths are even shorter than traditional C═N bond, which is attributed to the strong electrophilic ability of H atom on C3. An ordered chain structure is built by the hydrogen bonds between protic H atom/H atom in carboxyl and Br^- anion. Finally, a one-dimensional chain-like architecture is formed when the hydrogen bonds formed by Br^- anion with H atom on N2 and carboxyl, respectively (See Fig. S3).

3.3. Effect of catalysts

In order to explore the catalytic activity of nine aforementioned protic carboxyl imidazloium ILs, the model reaction of PO and CO_2 to afford propylene carbonate (PC) catalyzed by them is carried out in two reaction conditions: (1) 0.5 mol% catalyst under 120 °C and 1.5 MPa CO_2 pressure during 2.0 h; (2) 1.0 mol% catalyst under 80 °C and 1.0 MPa CO_2 pressure during 12.0 h. No co-catalyst and solvent are included in the whole catalytic process. The corresponding results are listed in Table 1.

The elongated alkyl chain length in cation is helpful to increase the catalytic activity. The product yield reaches the maximum when the substituted group is carboxypropyl. Then, the product yield is decreased with further elongation of alkyl chain length. The catalytic activity decreases in the order of HCPImCl (89%) > HCEImCl (86%) > HCBImCl (83%) > HCMImCl (74%) (entries 1–4). When the counterpart anion is the Br^- anion, there is the similar sequence, i.e., HCPImBr (92%) > HCEImBr (91%) > HCBImBr (89%) > HCMImBr (87%) (entries 5–8). The long alkyl chain length would weaken the interaction between carboxyl and anion leading to the stronger acidity, which is favorable for the nucleophilic activation. However, the steric hindrance would also be improved with the elongation of substituted alkyl chain length leading to the lower product yield. The product yield of HCBImBr not only is less than that of HCPImBr but also is less than that of HCEImBr. HCBImBr just displays better catalytic activity than HCMImBr. The suitable alkyl chain length (HCPImBr) is the more important item to enhance the catalytic activity. When the alkyl chain length is fixed, the catalytic activity would be increased with the improvement of nucleophilic activation and leaving ability of halogen anions, i.e., HCMImBr 87% > HCMImCl 74% (entries 1 and 5), HCEImBr 91% > HCEImCl 86% (entries 2 and 6), HCPImI 94% > HCPImBr 92% > HCPImCl 89% (entries 3, 7, and 9), HCBImBr 89% > HCBImCl 83% (entries 4 and 8). As compared with other reported carboxyl-based ionic liquids (See Table S3), reaction condition is not greatly refined. However, there are two highlights in this work including the less catalyst amount and the higher product yield.

Table 1
Catalytic activity of various catalysts[a].

Entry	Catalyst	Yield%[b]	TON	TOF/h^{-1}
1	HCMImCl	74	148	74
2	HCEImCl	86	172	86
3	HCPImCl	89	178	89
4	HCBImCl	83	166	83
5	HCMImBr	87	174	87
6	HCEImBr	91	182	91
7	HCPImBr	92	184	92
8	HCBImBr	89	178	89
9	HCPImI	94	188	94
10[c]	HCMImBr	60	60	5
11[c]	HCEImBr	82	82	7
12[c]	HCPImBr	85	85	7
13[c]	HCBImBr	63	63	5

[a] Reaction conditions: PO 100 mmol, catalyst 0.5 mol%, temperature 120 °C, CO_2 pressure 1.5 MPa, reaction time 2.0 h.

[b] Isolated yield.

[c] Reaction conditions: PO 50 mmol, catalyst 1.0 mol%, temperature 80 °C, CO_2 pressure 1.0 MPa, reaction time 12.0 h.

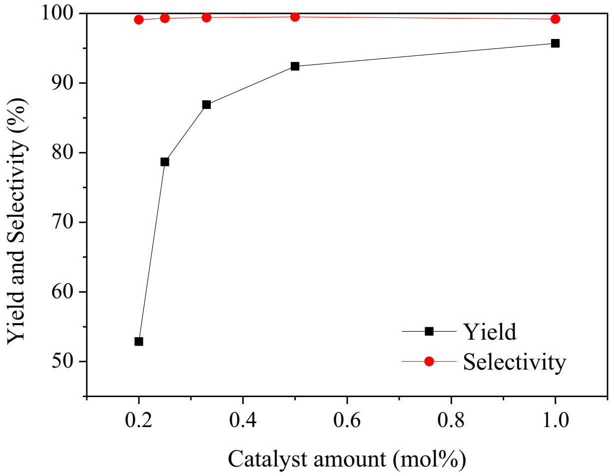

Fig. 2. Influence of catalyst amount on PC yield and selectivity (reaction conditions: PO 100 mmol, temperature 120 °C, CO_2 pressure 1.5 MPa, time 2.0 h).

In addition, the catalytic performance of four protic carboxyl imidazloium ILs is explored under more benign conditions, i.e., 1.0 mol% catalyst under 80 °C and 1.0 MPa CO_2 initial pressure during 12.0 h. The relative sequence among four ILs is kept under two different reaction conditions except that the PC yield is decreased under the latter reaction conditions. However, both reaction temperature and CO_2 initial pressure are greatly reduced, which are two important dangerous items in reaction. Moreover, 85% yield is also acceptable indicating that HCPImBr could keep high catalytic activity under mild reaction conditions.

3.4. Effect of reaction parameter

The HCPImBr has the highest catalytic activity, therefore, it is taken as an example to explore the influence of reaction parameters on catalytic activity including catalyst amount, reaction temperature, CO_2 pressure, and reaction time. Only one reaction parameter is varied while other three reaction conditions are fixed.

First, the influence of catalyst amount on synthesis of PC is investigated under 120 °C and 1.5 MPa CO_2 pressure during 2.0 h with 100 mmol PO. The corresponding results are shown in Fig. 2. In the whole investigated region, the PC yield increases with the enhance of HCPImBr amount. The sharp improvement of PC yields happens when the HCPImBr amount increases from 0.2 mol% (53%) to 0.5 mol% (92%). After that, the increased extent of PC yield is decreased with the further enhancement of HCPImBr amount up to 1.0 mol%. So catalyst amount of 0.5 mol% is selected for the following investigation with the best compromise between catalyst amount and PC yield.

Subsequently, the reaction temperature is another important factor in the catalytic process. The influence of reaction temperature on the PC yield is determined, and the

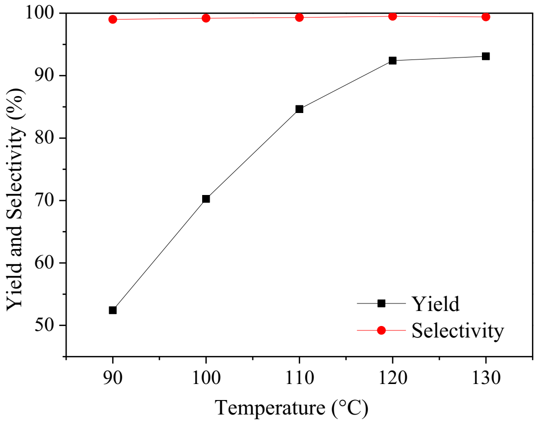

Fig. 3. Influence of reaction temperature on PC yield and selectivity (reaction conditions: PO 100 mmol, HCPImBr 0.5 mol%, CO_2 pressure 1.5 MPa, time 2.0 h).

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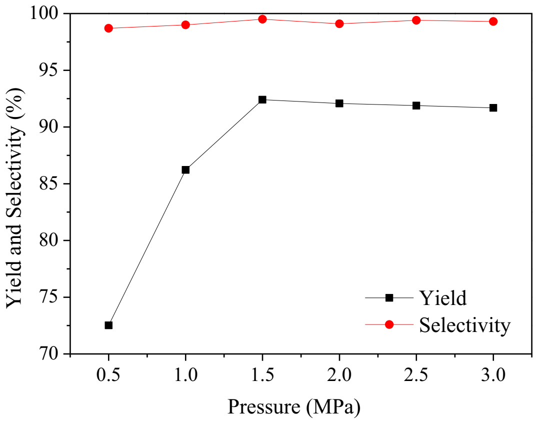

Fig. 4. Influence of CO_2 pressure on PC yield and selectivity (reaction conditions: PO 100 mmol, HCPImBr 0.5 mol%, temperature 120 °C, time 2.0 h).

result is shown in Fig. 3. The PC yield increases rapidly from 53% to 92% with the temperature increasing from 90 °C to 120 °C. When the reaction temperature is further increased to 130 °C, there is only a slight enhancement for PC yield. Therefore, the most optimal reaction temperature is 120 °C. It has been testified that the thermal decomposition temperature of HCPImBr is much higher than 200 °C suggesting that it would not decompose during the reaction process.

Next, the effect of CO_2 pressure on the PC yield is investigated (See Fig. 4). There is a turning point at the CO_2 pressure of 1.5 MPa. In contrast, the PC yield increases with the improvement of temperature and catalyst amount. Before 1.5 MPa, the PC yield increases gradually with the CO_2 pressure increasing. However, there is a slight decline of PC yield with the further increase of CO_2 pressure in the high-pressure region (1.5–3.0 MPa). There are two phases including a CO_2-rich phase of the top phase and the PO-rich phase in the bottom phase in the system [36]. The enhanced pressure would push more CO_2 into the reaction system to facilitate the reaction. However, the increased CO_2 pressure would also reduce the PO concentration in the bottom phase resulting in the less product yield. Therefore, CO_2 pressure of 1.5 MPa is the optimal pressure for synthesis of PC in the presence of HCPImBr. When the CO_2 pressure is enhanced, more CO_2 would dissolve in PO to form the CO_2-PO complex via the strong interaction. It would suppress the interaction between PO and ionic liquids resulting in the lower activity. Therefore, the product yield displays the slight decrease with the further enhancement of CO_2 pressure.

Finally, the effect of reaction time is explored. As shown in Fig. 5, The PC yield increases rapidly up to 92% within the first 2.0 h. Then, it keeps smooth when reaction time continues to be prolonged. In general, the optimal reaction conditions is under 120 °C, 1.5 MPa CO_2 pressure with 0.5 mol% catalyst amount for 2.0 h. In addition, the PC selectivity is kept above 99% throughout. In the investigated range, the product yield is enhanced with the increase of other reaction parameters, although sometimes the improved extent is not significant. However, the product yield would be decreased if an unsuitable CO_2 pressure is applied.

3.5. Recyclability of the catalyst

In order to test the catalyst reusability, the coupling reaction of CO_2 and PO is performed under the aforementioned optimal reaction conditions. When the reaction is finished, PC is removed from the reaction mixture under reduced pressure by distillation. HCPImBr is regenerated from the residue, which is washed by ethyl acetate. Subsequently, the catalyst is dried under vacuum to be reused for the next run. It can be seen that the catalyst could be utilized for five times with only slight loss of PC yield (See Fig. 6) suggesting that HCPImBr has good recyclability for the cycloaddition reaction of CO_2 and PO.

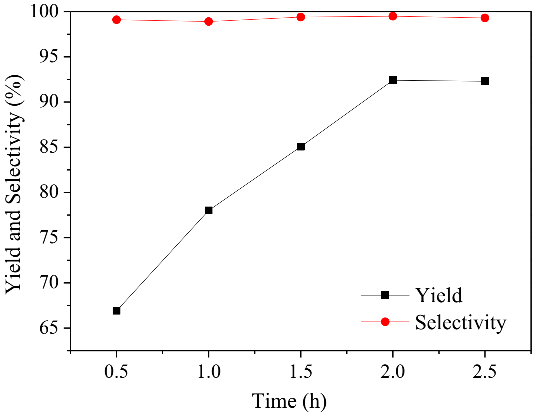

Fig. 5. Influence of reaction time on PC and selectivity (reaction conditions: PO 100 mmol, HCPImBr 0.5 mol%, temperature 120 °C, CO_2 pressure 1.5 MPa).

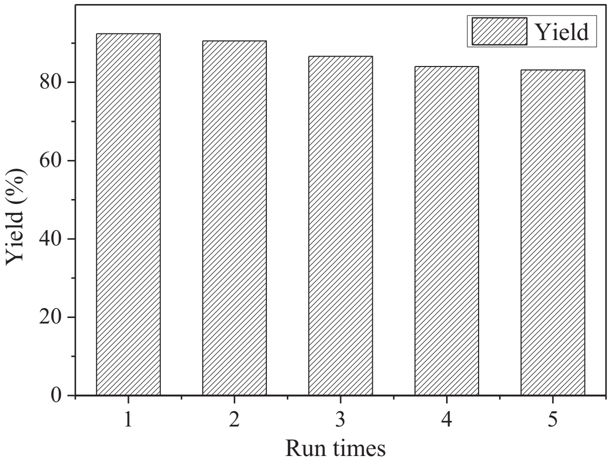

Fig. 6. Recyclability of HCPImBr (reaction conditions: PO 100 mmol, HCPImBr 0.5 mol%, temperature 120 °C, CO_2 pressure 1.5 MPa, time 2.0 h).

3.6. Catalytic activity toward other epoxides

The generality of catalyst is another important item to evaluate the performance of catalyst. HCPImBr is investigated to catalyze the cycloaddition reaction of CO_2 with various epoxides under the above determined optimal reaction conditions and the corresponding results are summarized in Table 2. HCPImBr exhibits excellent catalytic activity for most of epoxides (entries 1–7) with acceptable cyclic carbonates yields above 80% associated with selectivity larger than 99%. The yield of 1 h is the lowest in several investigated epoxides, which is consistent with previous report catalyzed by other ionic liquids. Even if the reaction temperature is increased to 130 °C and the reaction time is extended to 12.0 h, the product yield of cyclohexene carbonate is only 53%. The large steric hindrance of cyclohexene oxide greatly impedes the nucleophilic activation from anion resulting in the low product yield. Meanwhile, it is also testified that the nucleophilic activation is the other important item to promote the ring-opening of PO.

3.7. Reaction mechanism

3.7.1. Single-IL model

To provide helpful information for the synthesis of ionic liquid in future, the reaction mechanism of CO_2 and PO is further explored at the B3PW91/6-31G(d,p) level [37–39]. All the electronic calculations are performed in the Gaussian 09 program [40]. The HCPImCl is chosen as the example to confirm the possible reaction routes. It is well known that there are three steps for the whole process, ring-opening of PO, CO_2 insertion, and ring-closure to produce PC. The ring-opening of PO is promoted by the nucleophilic activation from Cl^- anion along with the electrophilic activation from the alive H atoms in cation. Therefore, the protic hydrogen atom (H1), the hydrogen atom in carboxyl group (H2), and hydrogen atom in imidazole ring (H3) would be taken as the electrophile. One of hydrogen atoms is in charge of the electrophilic activation while another hydrogen atom is in charge of stabilizing the Cl^- anion by hydrogen bond. Six possible routes are confirmed according to the different ring-opening steps (See Table S4). Since other two steps are not rate-determining steps, they are not stated out in this work.

The H2 atom activates the O atom of PO and the H1 atom forms hydrogen bond with Cl^- anion (route S-HCPImCl-1, S indicating Single-IL model, 1 indicating the first route in this model, other routes are named following the same rule). The role of above two hydrogen atoms are exchanged resulting in route S-HCPImCl-2. The H1 atom would also be combined with the H3 atom leading to route S-HCPImCl-3 and route S-HCPImCl-4. And so on, the H3 atom would be cooperated with the H2 atom leading to route S-HCPImCl-5 and route S-HCPImCl-6. The corresponding optimized structures for transition states are plotted in Table S4 along with the barrier height. The barrier heights are corrected at the M06/6-311+G(2d,2p) level [39,41] on the basis of the optimized geometries along with polarized continuum model (PCM) [42,43]. It is unfortunate that route S-HCPImCl-6 is not successfully located. For other five routes, the barrier height of route S-HCPImCl-2 is the lowest indicating the most favorable route. Following the same activating method, the transition states of ring-opening step catalyzed by other three ionic liquids, HCMImCl, HCEImCl, and HCBImCl are determined. The corresponding optimized structures for transition states are plotted in Table S5 along with the barrier height. The barrier heights decrease in the sequence of route S-HCBImCl-2 (17.22 kcal/mol) > route S-HCMImCl-2

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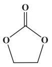
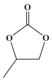
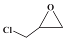
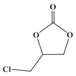
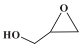
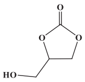
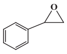
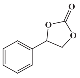
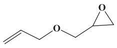
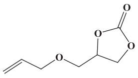
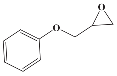
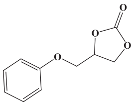
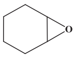
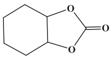
Table 2
Cycloaddition reaction of CO_2 and various epoxides catalyzed by HCPImBr.

Entry	Epoxide	Cyclic carbonate	Selectivity (%)	Yield[b] (%)
1	 **1a**	 **2a**	>99	95
2	 **1b**	 **2b**	>99	92
3	 **1c**	 **2c**	>99	84
4	 **1d**	 **2d**	>99	87
5	 **1e**	 **2e**	>99	82
6	 **1f**	 **2f**	>99	83
7	 **1g**	 **2g**	>99	83
8[c]	 **1h**	 **2h**	>99	53

[a] Reaction conditions: epoxides 100 mmol, catalyst HCPImBr 0.5 mol%, CO_2 pressure 1.5 MPa, reaction time 2.0 h, temperature 120 °C.
[b] Isolated yield.
[c] Reaction conditions:temperature 130 °C, reaction time 12.0 h.

(13.28 kcal/mol) > route S-HCPImCl-2 (12.92 kcal/mol) > route S-HCEImCl-2 (12.13 kcal/mol), which is not consistent with the experimental result listed in Table 1. Moreover, it does not follow the variation sequence of substituted alkyl chain length. To obtain more reliable result, the mechanism is studied by Double-IL mode again.

3.7.2. Double-IL model

HCPImCl is still taken as the example to explore the mechanism. Thirty three routes are designed according to the different electrophilic activation modes. It is better to employ as much as possible hydrogen atoms to activate the PO. However, two hydrogen atoms would simultaneously activate the oxygen atom of PO at most due to the steric hindrance. Six routes, route D-HCPImCl-1-route D-HCPImCl-6 (See Table S6, route D-HCPImCl-1, D indicating Double-IL model, 1 indicating the first route in this model, other routes are named following the same rule), are finally located by combination of two hydrogen atoms to activate the PO. Another situation is that only one HCPImCl is utilized to activate the PO, then, the other one is to stabilize the attacking HCPImCl. In the other word, only one HCPImCl enters the catalytic center region. In the catalytic center region, three active hydrogen atoms would activate the PO in succession. When the attacking HCPImCl is fixed, the other HCPImCl would utilize different hydrogen atoms to form hydrogen bonds with the first one. As a result, eighteen routes (route D-HCPImCl-7-route D-HCPImCl-24) are designed, which is plotted in Table S7. Finally, two HCPImCl and PO form an intermediate, in which one HCPImCl is taken as the electrophile, while the other one is taken as the nucleophile. When the first one is fixed, the other one is turned over to get the different routes. Nine possible routes are located (route D-HCPImCl-25-route D-HCPImCl-33, See Table S8). In the third situation, the most favorable route has the barrier height of 8.38 kcal/mol. Moreover, it is also the most popular route in all of routes. Following the same mechanism, the mechanism of ring-opening step catalyzed by other catalysts is considered. The corresponding energy profiles are plotted in Fig. 7 along with the optimized structures of transition states. The barrier heights decrease in the sequence of route D-HCMImCl (24.74 kcal/mol) → route D-HCBImCl (14.68 kcal/mol) → route D-HCEImCl (13.38 kcal/mol) → route D-HCPImCl (8.38 kcal/mol), which is totally consistent with the experimental product yields of HCMImCl (74%) → HCBImCl (83%) → HCEImCl (86%) → HCPImCl (89%). The catalytic activity enhances with the increase of alkyl chain length. When the substituted group is carboxypropyl, the catalytic activity is the highest. After that, the catalytic activity is decreased, which is assigned to the larger steric hindrance. The carboxypropyl chain length is the best choice for protic carboxyl imidazolium ionic liquids.

4. Conclusions

Nine protic carboxyl imidazolium ILs exhibit excellent catalytic activity for the synthesis of cyclic carbonates with the product yield over 80% in the absence of co-catalyst and solvent. HCPImBr presents the best catalytic activity among them achieving the product yield of 92%. Even if the temperature and CO_2 pressure are decreased to 80 °C and 1.0 MPa, the 85% product yield would be acquired by HCPImBr. The optimal reaction conditions are confirmed to be 120 °C, 1.5 MPa CO_2 initial pressure with 0.5 mol% HCPImBr amount during 2.0 h. After five runs, the stable product yield is kept under the optimal reaction conditions. The determined catalytic activity on the basis of barrier height is consistent with the variation of product yield. Both the theoretical and experimental results show that the suitable alkyl chain would promote the ring-opening of PO.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

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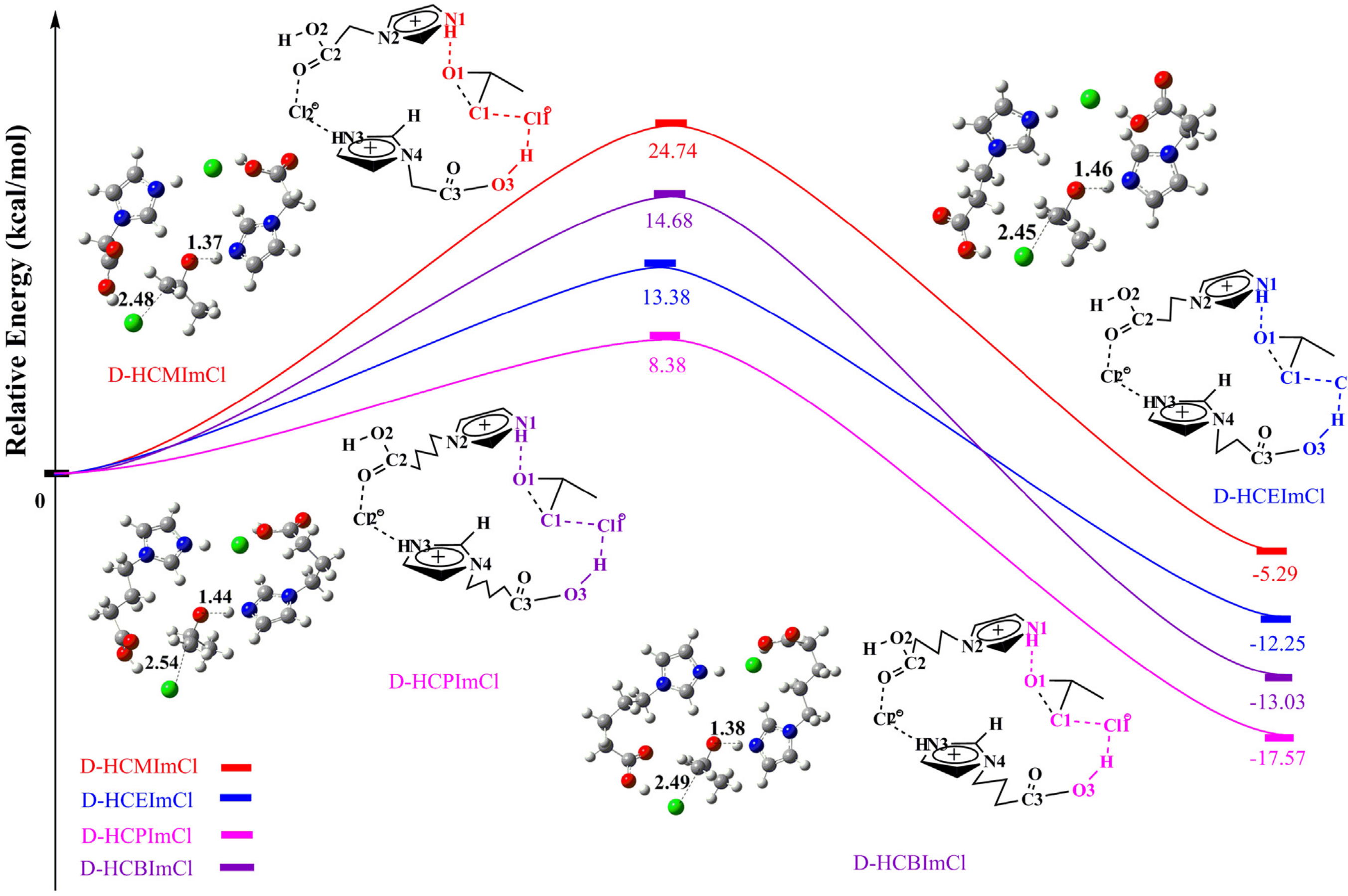

Fig. 7. The corresponding energy profiles along with the schematic structures of transition states calculated at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level.

softwares. This work was supported by the National Natural Science Foundation of China (21476061, 21676071, 21703053, 21975064), and the Excellent Foreign Experts Project of Henan University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2019.111936.

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