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Dialkylpyrazolium ionic liquids as novel catalyst for efficient fixation of CO_2 with metal- and solvent-free

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Graphic Abstract



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Highlights

- Dialkylpyrazolium ILs are firstly used as catalysts for the fixation of CO₂.
- Good yields are achieved under a mild condition without solvent or co-catalyst.
- The mechanism with a synergistic effect is found to promote the reaction.
- They would be reused by five times without decrease of catalytic activity.

Abstract

The efficient fixation of CO_2 without co-catalyst and solvent under metal-free condition is still an urgent topic in sustainable chemistry. In this work, a series of dialkylpyrazolium ionic liquids are employed to promote the cycloaddition of CO_2 and PO to produce PC. They would be easily synthesized by a simple one-pot reaction. The effect of alkyl chain length in cation and different anion is explored. Diethylpyrazolium iodide presents the excellent catalytic activity with the product yield of 96% and selectivity of 99% in a benign condition. Moreover, the catalyst could be reused for at least five times without significant loss of catalytic activity. An intensive structure-activity research testifies that the cycloaddition of CO_2 with PO is activated by a synergistic effect from both cation and anion of ILs. To confirm it, the detailed mechanism is investigated by density functional theory associated with the non-covalent interactions and atoms in molecule analysis. Besides the electrostatic interaction between cation of ionic liquid and PO, the noncovalent interaction, especially for hydrogen bond, plays a vital role in promoting the reaction.

Keywords: dialkylpyrazolium ionic liquids; CO₂; cycloaddition reaction; structure-activity relationship; DFT;

1 Introduction

With the rapid development of economy and industrialization process, the fossil fuels are gradually depletion. Carbon dioxide (CO₂) is inexpensive, nontoxic, abundant, and renewable C1 resource in the world. Many efforts have been made to convert CO₂ to useful chemical products including methane [1], carboxylic acid [2], hydrocarbon [3], and cyclic carbonate [4]. The cyclic carbonate has been widely applied in numerous regions, such as electrolytes of Li ion batteries [5], aprotic polar solvents [6], degreasing agents [7], and valuable monomers of polycarbonates and

polyurethanes [8]. Up to date, the cycloaddition of CO_2 with epoxides is regarded as one of the most efficient methods to synthesize cyclic carbonate because of the 100% atom utilization and negligible side product. However, the thermo stability and kinetic inertness of CO_2 greatly impede its large scale application [9]. Although numerous catalysts have been developed, such as, modified molecular sieves [10], metal oxide [11], transition metal complexes [12] and ionic liquids (ILs) [13], they confront some common shortcomings including the requirement of co-catalyst and organic solvent, harsh reaction condition, and others [14,15]. It is still an urgent problem to develop single-component catalyst to activate the chemical fixation of CO_2 with high efficiency.

Recently, ionic liquids have become a hotspot in catalytic region because of their special structure and properties [16]. Moreover, they are also an excellent solvent. Many ionic liquids have been employed as effective catalysts with metal- and solvent-free to activate the cycloaddition of CO_2 with epoxides [17]. Imidazolium ionic liquids, as one of the most popular catalysts, have attracted extensive experimental and theoretical attentions [18]. As their structural isomer, fewer investigations have been focused on pyrazolium ionic liquids. In 1983, dimethylpyrazolium iodide (DMPzI) was firstly synthesized by Claramunt et al [19]. Later, Enrique et al. have synthesized dibutylpyrazolium iodide (DBPzI) by microwave radiation heating [20]. After that, Huynh et al. have synthesized diethylpyrazolium bromide (DEPzBr) and used it to prepare N-heterocyclic carbene complexes [21]. However, their catalytic activity for the conversion of CO_2 has never been investigated.

In this work, they are firstly employed to accelerate the cycloaddition of CO₂ with epoxides. In addition, other twelve pyrazolium ionic liquids are also synthesized to explore the influence of different alkyl chain length and anions on the catalytic performance. Moreover, the effect of catalyst loading, initial CO₂ pressure, reaction temperature, and reaction time is studied to confirm the optimal reaction condition. The reusability and generality of diethylpyrazolium iodide (DEPzI) is also considered. Finally, the reaction mechanism is elucidated by density functional theory (DFT) to uncover the difference of various catalysts from the micro viewpoints. It is expected that pyrazolium ionic liquids would become a new focus in catalytic field after imidazolium ionic liquids. Combination of theoretical and experimental studies would open an express pathway to search for efficient and single-component ionic liquids to

promote the chemical fixation of CO₂ in a proper condition.

2 Experimental section

2.1 Instruments and Reagents

Fourier transform infrared (FT-IR) spectra were collected on Bruker Vertex 70 spectrometer (KBr disks). HR-MS was determined with Agilent 1290 Infinity LC with 6224 TOF MSD. MS was determined by Bruker AmaZon SL (ESI) mass spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100MHz) spectra were recorded on Bruker Avance III HD spectrometer with the presence of tetramethylsilane as an internal standard. The melting point was tested by using a differential scanning calorimeter (Mettler Toledo DSC851e) in the temperature range from 0°C to 200°C and the thermal decomposition temperature was analyzed with a thermal gravimetric analyzer (Mettler Toledo TGA/SDTA851e). Elemental analyses were performed on a Vario EL cube elemental analyzer. GC analyses were performed on Agilent GC-7890B using a flame ionization detector.

The pyrazole and halohydrocarbon were purchased from Macklin Biochemical Co., Ltd. Propylene oxide (PO), styrene oxide, epoxy chloropropane, and ethylene oxide were purchased from Aladdin Co. Other commonly used chemical regents were produced by Sinopharm Chemical Reagent Co., Ltd. CO₂ (99.9% purity) were purchased from Kaifeng Xinri Gas Co. All reactants were used directly as received without any further purification.

2.2 Preparation of pyrazolium ionic liquids

These dialkylpyrazolium ionic liquids were prepared according to the literature [21] with some revision. The typical synthesis procedure of dialkylpyrazolium ILs is shown in Scheme 1. 1,2-Diethylpyrazolium Iodide (DEPzI): In a three-necked bottle, pyrazole (10 mmol) and powdered KOH (10 mmol) were added into 10 mL CH₃CN and the mixture was stirred at ambient temperature for 1 h. Then ethyl iodide (24 mmol) was added to reactants and the reaction was continued for 24 h under reflux conditions. After the reaction, the volatiles were removed under reduced pressure. CH₂Cl₂ was added to the residue and the resulting suspension was filtered. The solvent of the filtrate was removed by vacuum distillation, and the resulting residue was subsequently washed with ethyl acetate to give a yellow solid. After removing the moisture by cyclohexane reflux, the pure DEPzI was obtained: 1.162 g, yield 46%, m.p: 140.3°C. *T*m (decomposition temperature of 10% weight loss): 201.1°C. ¹H NMR (400 MHz, CDCl₃): δ 8.48-8.40 (d, *J* = 3.0 Hz, 2H, Py-H), 6.79 (t, *J* = 3.0 Hz, Py-H), 6.79 (

1H, Py-H), 4.86-4.79 (q, J = 7.3 Hz, 4H, -NCH₂), 1.69 (t, J = 7.3 Hz, 6H, -CH₃). ¹³C NMR (100 MHz, D₂O): δ 135.82 (s, N-CH), 107.43 (s, CH), 45.40 (s, N-CH₂), 13.40 (s, -CH₃). Anal. Calcd for C₇H₁₃N₂I: C, 33.33; H, 5.159; N, 11.11. found: C, 33.66; H, 5.375; N, 10.80. MS (ESI): m/z 125.14 [C₇H₁₃N₂⁺]; 127.04 [I⁻].

Other dialkylpyrazolium iodide and bromide were synthesized with the identical procedure for DEPzI.

1,2-Dimethylpyrazolium Iodide (DMPzI). White solid (51%); m.p: 194.0°C. (lit^[19]: 186-187°C). *T*m: 201.4°C. ¹H NMR (400 MHz, D₂O): δ 8.02 (d, *J* = 2.9 Hz, 2H, Py-H), 6.60 (td, *J* = 3.0 Hz, 1H, Py-H), 3.99 (s, *J* = 1.2 Hz, 6H, N-CH₃). ¹³C NMR (100 MHz, D₂O): δ 137.42 (s, N-CH), 107.00 (s, CH), 36.44 (s, -CH₃). Anal. Calcd for C₅H₉N₂I: C, 26.79; H, 4.018; N, 12.50. found: C, 26.35; H, 3.848; N, 12.29. MS (ESI): *m/z* 97.30 [C₅H₉N₂⁺].

1,2-Dipropylpyrazolium Iodide (DPPzI). Yellow solid (43%); m.p: 83.7°C. *T*m: 199.6°C. ¹H NMR (400 MHz, D₂O): δ 8.07 (d, *J* = 3.0 Hz, 2H, Py-H), 6.62 (t, *J* = 3.0 Hz, 1H, Py-H), 4.27 (t, *J* = 7.3 Hz, 4H, N-CH₂), 1.79 (m, *J* = 7.4 Hz, 4H, -CH₂-), 0.80 (t, *J* = 7.4 Hz, 6H, -CH₃). ¹³C NMR (100 MHz, D₂O): δ 136.87 (s, N-CH), 107.28 (s, CH), 51.35 (s, N-CH₂), 21.98 (s, -CH₂-), 9.81 (s, -CH₃). Anal. Calcd for C₉H₁₇N₂I: C, 38.57; H, 6.071; N, 10.00. found: C, 38.58; H, 6.316; N, 10.03. MS (ESI): *m/z* 153.07 [C₉H₁₇N₂⁺].

1,2-Dibutylpyrazolium Iodide (DBPzI). Yellow solid (42%); m.p: 71.4°C. *T*m: 195.8°C. ¹H NMR (400 MHz, D₂O): δ 8.11 (d, *J* = 2.9 Hz, 2H, Py-H), 6.67 (t, *J* = 3.0 Hz, 1H, Py-H), 4.35 (t, *J* = 7.4 Hz, 4H, N-CH₂), 1.80 (m, *J* = 7.5 Hz, 4H, -CH₂-), 1.27 (m, *J* = 7.4 Hz, 4H, -CH₂-), 0.84 (t, *J* = 7.4 Hz, 6H, -CH₃). ¹³C NMR (100 MHz, D₂O): δ 136.73 (s, N-CH), 107.29 (s, CH), 49.76 (s, N-CH₂), 30.27 (s, -CH₂-), 18.84 (s, -CH₂-), 12.65 (s, -CH₃). Anal. Calcd for C₁₁H₂₁N₂I: C, 42.86; H, 6.818; N, 9.09. found: C, 42.93; H, 6.807; N, 8.94. MS (ESI): *m/z* 181.06 [C₁₁H₂₁N₂⁺].

1,2-Diamylpyrazolium Iodide (DAmPzI). Yellow solid (33%); m.p: 75.7°C. *T*m: 195.0°C. ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, *J* = 2.9 Hz, 2H, Py-H), 6.78 (t, *J* = 2.9 Hz, 1H, Py-H), 4.72 (t, *J* = 7.5 Hz, 4H, N-CH₂), 1.96 (m, *J* = 7.4 Hz, 4H, -CH₂-), 1.41 (m, *J* = 6.1, 3.3, 2.6 Hz, 8H, -CH₂-), 0.88 (t, 6H, -CH₃). HR-MS (QTOF) calcd. for C₁₃H₂₅N₂I (*m*/*z*): 209.2018, found: 209.1985.

1,2-Diethylpyrazolium Bromide (DEPzBr). Yellow solid (47%); ¹H NMR (400 MHz, D₂O): δ 8.10 (d, J = 3.0 Hz, 2H, Py-H), 6.67 (t, J = 3.0 Hz, 1H, Py-H), 4.37 (q, J = 7.3 Hz, 4H, N-CH₂), 1.46 (t, J = 7.2 Hz, 6H, -CH₃). MS (ESI): m/z 125.14

 $[C_7H_{13}N_2^+]$, 81.80 $[Br^-]$.

1,2-Dipropylpyrazolium Bromide (DPPzBr). Yellow solid (43%); ¹H NMR (400 MHz, D₂O): δ 8.07 (d, *J* = 3.0 Hz, 2H, Py-H), 6.62 (t, *J* = 3.0 Hz, 1H, Py-H), 4.27 (t, *J* = 7.3 Hz, 4H, N-CH₂), 1.79 (q, *J* = 7.4 Hz, 4H, -CH₂-), 0.80 (t, *J* = 7.4 Hz, 6H, -CH₃). MS (ESI): *m*/*z* 153.07 [C₉H₁₇N₂⁺].

1,2-Dibutylpyrazolium Bromide (DBPzBr). Yellow solid (42%); ¹H NMR (400 MHz, D₂O): δ 8.15 (d, *J* = 2.9 Hz, 2H, Py-H), 6.70 (t, *J* = 3.0 Hz, 1H, Py-H), 4.38 (t, *J* = 7.4 Hz, 4H, N-CH₂), 1.87-1.77 (m, 4H, -CH₂-), 1.29 (m, *J* = 7.4 Hz, 4H, -CH₂-), 0.86 (t, *J* = 7.4 Hz, 6H, -CH₃). MS (ESI): *m*/*z* 181.06 [C₁₁H₂₁N₂⁺].

1,2-Diamylpyrazolium Bromide (DAmPzBr). Yellow solid (33%); ¹H NMR (400 MHz, D₂O): δ 8.07 (d, *J* = 3.0 Hz, 2H, Py-H), 6.63 (t, *J* = 3.0 Hz, 1H, Py-H), 4.31 (t, *J* = 7.4 Hz, 4H, N-CH₂), 1.83-1.73 (m, 4H, -CH₂-), 1.19 (tt, *J* = 5.2, 2.5 Hz, 8H, -CH₂-), 0.76-0.70 (t, 6H, -CH₃). MS (ESI): *m/z* 209.08 [C₁₃H₂₅N₂⁺].

1,2-Dihexylpyrazolium Bromide (DHPzBr). White solid (25%); m.p: 94.2°C. *T*m: 185.8°C. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, *J* = 2.9 Hz, 2H, Py-H), 6.75 (t, *J* = 2.8 Hz, 1H, Py-H), 4.73 (t, *J* = 7.5 Hz, 4H, N-CH₂), 1.94 (q, *J* = 7.4 Hz, 4H, -CH₂-), 1.42 (h, *J* = 6.2, 4.4 Hz, 4H, -CH₂-), 1.32 (tt, *J* = 8.8, 5.0 Hz, 8H, -CH₂-), 0.94-0.84 (m, 6H, -CH₃). HR-MS (QTOF) calcd. for C₁₅H₂₉N₂Br (*m*/*z*): 237.2331, found: 237.2338.

1,2-Dioctylpyrazolium Bromide (DOPzBr). White solid (18%); m.p: 112.4°C. Tm: 186.0°C. ¹H NMR (400 MHz, DMSO-*d*6): δ 8.60 (d, J = 2.9 Hz, 2H, Py-H), 6.93 (t, J = 2.9 Hz, 1H, Py-H), 4.47 (t, J = 7.4 Hz, 4H, N-CH₂), 1.82 (p, J = 7.2 Hz, 4H, -CH₂-), 1.27 (dd, J = 11.4, 5.7 Hz, 20H, -CH₂-), 0.89-0.83 (t, 6H, -CH₃). HR-MS (QTOF) calcd. for C₁₉H₃₇N₂Br (*m*/*z*): 293.2957, found: 293.2962.

1,2-Didecylpyrazolium Bromide (DDePzBr). White solid (13%); m.p: 115.5°C. *T*m: 184.8°C. ¹H NMR (400 MHz, DMSO-*d*6): δ 8.57 (d, *J* = 2.9 Hz, 2H, Py-H), 6.93 (t, *J* = 2.9 Hz, 1H, Py-H), 4.45 (t, *J* = 7.4 Hz, 4H, N-CH₂), 1.80 (s, 4H, -CH₂-), 1.26 (d, *J* = 13.5 Hz, 28H, -CH₂-), 0.88-0.84 (t, 6H, -CH₃). HR-MS (QTOF) calcd. for C₂₃H₄₅N₂Br (*m*/*z*): 349.3583, found: 349.3679.

1,2-Didodecylpyrazolium Bromide (DDoPzBr). White solid (11%); m.p: 117.2°C. Tm: 188.1°C. ¹H NMR (400 MHz, CDCl₃): δ 8.58 (d, *J* = 2.9 Hz, 2H, Py-H), 6.74 (t, *J* = 2.9 Hz, 1H, Py-H), 4.73 (t, *J* = 7.5 Hz, 4H, N-CH₂), 1.93 (p, *J* = 7.5 Hz, 4H, -CH₂-), 1.48-1.18 (m, 32H, -CH₂-), 0.88 (t, *J* = 6.8 Hz, 6H, -CH₃). HR-MS (QTOF) calcd. for C₂₇H₅₃N₂Br (*m*/*z*): 405.4209, found: 405.4272.

1,2-Diethylpyrazolium tetrafluoroborate (DEPzBF₄). 10 mmol DEPzI and 12 mmol NaBF₄ was suspended in 10mL acetone and stirred at 60°C for 6 h. After the reaction, the mixture was filtered and the solvent of filtrate was removed, then the product was dried under vacuum. Yellow solid (76%): MS (ESI): m/z 87.83 [BF₄⁻].

1,2-Diethylpyrazolium hexafluorophosphate (DEPzPF₆). 10 mmol DEPzI were dissolved in 30mL distilled water, then 10 mmol KPF₆ were added in batches, small white crystal has been generated immediately, reaction continues to stir for 5 h and the mixture was filtered and the residue was washed with water until no precipitation formation with AgNO₃, the product was dried under vacuum. Yellow solid (42%): MS (ESI): m/z 144.99 [PF₆⁻]. Both DEPzBF₄ and DEPzPF₆ were verified by silver nitrate solution, there were no apparent precipitations. And almost no iodide ion peak was appeared in the mass spectrum indicating the high purity (>99%) of two ILs. 2.3 Cycloaddition reaction of CO₂ with epoxides

An epoxide/catalyst mixture was introduced in the high pressure cell (100 mL) at ambient temperature, then CO₂ (1.0-3.0 MPa) was added to the cell and heated up to the desired temperature. The reaction was stirred at 90-140°C for 1-5 h. After this reaction, the reactor was cooled to room temperature in an ice-water bath and the pressure was released. The autoclave was opened, and the isolated yields were calculated from the weight of product (combination of cyclic carbonate and starting material only, or (as indicated) by the weight of isolated product after column chromatography. Some reactions were repeated and the reproducibility of yields was \pm 3%). The structures of cyclic carbonates were characterized by ¹H NMR. In order to verify the reliability of isolated yield and detect the selectivity, the product yields of some reactions were analyzed on GC.

3 Results and discussion

3.1 Synthetic and property of ILs

Fifteen dialkylpyrazolium ILs with different alkyl chain and anions have been easily synthesized with a one-pot alkylation reaction. DEPzBF₄ and DEPzPF₆ are synthesized by anion exchange reaction on the basis of DEPzI (Scheme 1). Among them, DMPzI, DEPzBr, and DBPzI have been reported, while others are firstly synthesized by us. In order to improve the product yield, KOH is added to the mixture as acid-binding agent. In the post-processing course, the moisture was removed by cyclohexane reflux, which could effectively purify the product. The structures of all ionic liquids have been characterized by ¹H NMR, ¹³C NMR, HR-MS, and elemental

analysis. The yields of dialkylpyrazolium ILs are reduced with the increase of chain length, which is attributed to the large steric hindrance of long alkyl chain. Additionally, the low yield of ionic liquids is aroused by introduction of two alkyl chains into the pyrazolium cation.

The thermal stability of five representative dialkylpyrazolium ILs are investigated by thermogravimetric analysis (TGA) (See Fig. 1). All of them present good thermal stability since the degradation started in a range of 195-201°C. The ILs have one-stage decomposition behaviors and the decomposition temperature is gradually reduced with increase of alkyl chain length. Moreover, there is no distinct mass loss below 200°C, which also justify the excellent purity of synthetic ILs. The dialkylpyrazolium ILs would be changed absolutely to gaseous products by thermal decomposition since they are decomposed in higher temperature with nearly zero weight percentage.

3.2 Effect of catalyst

The synthesized dialkylpyrazolium ionic liquids are tested as catalyst for the synthesis of propylene carbonate (PC) via the model reaction of propylene oxide (PO) with CO₂ under solvent-free condition without adding any co-catalyst. The results were summarized in Table 1. The formation of PC is not observed without any catalyst (entry 1) indicating that the cycloaddition of CO₂ with PO is difficult to be performed without catalyst even during 8 h reaction time. There is almost no catalytic activity with the existence of KBr during the same time. Acceptable yields of PC are observed when dialkylpyrazolium iodides are employed as catalysts (entries 3-7) during only 4 h. Among them, DEPzI is found to be the most active with the highest product yield of 91.2% (entry 4). In contrast, DMPzI has the lowest activity with the lowest product yield (83.3%, entry 3), while DPPzI, DBPzI, and DAmPzI have the similar catalytic activity with almost the same product yield (around 89%, entries 5-7). To further investigate the influence of alkyl chain length on catalytic activity, a series of dialkylpyrazolium bromide are synthesized and used as catalysts (entries 8-15). When alkyl chain length increases from DEPzBr to DPPzBr, there is a slight decrease in the product yield (entries 8-9). After that, the product yield is almost not varied from DPPzBr to DAmPzBr (entries 9-11). However, there is obvious decrease when the alkyl chain length is up to DHPzBr (entry 12). The product yield fluctuates in a range of 73.9%-80.3% with further elongation (entries 12-15). In general, the product yield presents stepped variation with the elongation of alkyl chain length. The larger

steric bulk of longer alkyl chain length would obstruct the electrophilic attack resulting in the less activity. However, the larger bulk of pyrazolium cation would also weaken the electrostatic interaction between cation and anion, which renders the counter halide more nucleophilicity. Consequently, there is not obvious reduction of product yield. The variation order of dialkylpyrazolium bromide is similar with that of dialkylpyrazolium iodide except that the product yields catalyzed by the latter are higher, which is attributed to their different anions.

The product yields decrease in the order of DEPzI (entry 4) > DEPzBr (entry 8) > DEPzBF₄ (entry 16) > DEPzPF₆ (entry 17), which is consistent with the nucleophilic and leaving ability of anions. The larger bulk of BF_4^- and PF_6^- anions would impede the nucleophilic attack resulting in the poor activity. In the other word, anion plays an important role in catalytic process.

The product yields catalyzed by DEPzI (entry 4) and DEPzBr (entry 8) are also confirmed by the GC method. Although the absolute product yields are improved, their relative order is still kept. The relative sequence of isolated yield is reliable, which would be increased if GC analysis method is employed to determine the product yield.

As compared with DEImI (entry S2) (See Table S1), DEPzI (entry S1) presents better product yield and TOF under the same reaction condition. Since they have the same anion, the different product yield should be attributed to their different cation. Moreover, the catalytic performance of DEPzI is better than that of TBAI (entry S3) [22], although the latter reaction is performed under higher temperature and during longer time. In contrast, the product yield of DEPzI is much less than that of HBetI (entry S4) [23] and HEMImI (entry S5) [24] and comparable to that of other task specific ionic liquids (entries S6-S8) [25-27]. It is worth to note that the reaction temperature and initial CO₂ pressure for CEMImBr (entry S6) is even lower than that for DEPzI indicating the high catalytic activity for the former. Incorporation of functional group is an efficient pathway to improve the catalytic performance. It is reasonable to believe that the higher product yield or milder reaction condition would be expected if the functional group is incorporated into the pyrazolium cation, which would be better than DEPzI (entry S1).

3.3 Effect of reaction conditions

In the following discussion, DEPzI is selected for further investigation because of its highest catalytic activity for cycloaddition of CO_2 with PO. The effect of

catalyst loading, initial CO₂ pressure, reaction temperature, and reaction time on the catalytic activity is explored one by one.

First, the influence of catalyst loading on PC yields is investigated under identical reaction conditions (See Fig. 2). The PC yield is sharply increased from 44% to 94.4% with the increase of DEPzI loading from 0.2 mol% to 1.0 mol%. After that, the further increase of DEPzI amount only leads to a slight enhancement of PC yield indicating that the optimal catalyst amount is 1.0 mol%. DEPzI could exhibit high activity under a low catalyst amount (1.0 mol%). Moreover, the PC selectivity is almost impervious (>99%) under catalyst loading from 0.2 mol% to 1.0 mol%. The 99% selectivity rather than 100% should be attributed to the generation of few possible by-products including acetone or 1,2-propylene diol [28].

Next, the influence of initial CO₂ pressure on the yield and selectivity of PC is studied (See Fig. 3). The PC yield dramatically increases from 70.1% to 94.4% when the initial CO₂ pressure increases from 1 MPa to 2 MPa. But there is mild decline by further incensement of initial CO₂ pressure to 3 MPa. The high initial CO₂ pressure would aggrandize CO₂ concentration in the liquid phase of reaction system leading to higher product yield. However, the higher CO₂ pressure puts more PO into the gas phase. Consequently, the concentration of PO around ILs is reduced, which is not favorable for the reaction since it is also a substrate [29]. The relative lower CO₂ pressure presents more potential industrial application [30,31]. Moreover, the PC selectivity is independent with CO₂ pressure with above 99% throughout.

Third, the influence of reaction temperatures on PC yield and selectivity is considered (See Fig. 4). The reaction is difficult to be carried out at 90°C with PC yield less than 50%. The PC yield increases greatly with the temperature increasing from 90°C to 120°C. Under the experimental conditions, a good yield (91.2%) could be reached at 120°C. The product yield would be increased to 94.4% at 130°C. When the temperature is higher than 130°C, there is no significant increase for PC yield. The selectivity of PC has almost no changes in the whole process. Meanwhile, the decomposition temperature of DEPzI is higher or close to 200°C in TGA analysis, which certifies the catalyst is stable at reaction temperature (130°C).

Finally, the effects of reaction time on PC yield and selectivity are shown in Fig. 5. The PC yield increases rapidly up to 94.4% within the first 4 h. Then, there is only a mild enhancement when another hour is prolonged. The PC selectivity is >99% throughout. In general, the optimal reaction condition is under 130°C, 2 MPa initial

CO₂ pressure and 4 h with 1 mol% catalyst loading.

3.4 Catalyst recycling

The catalyst reusability is also an important criterion to judge the performance of homogeneous catalyst. To test the catalyst reusability, the reaction of PO with CO_2 is performed under the optimal reaction conditions. After the catalytic reaction, the mixture is distilled under reduced pressure to remove large amounts of propylene carbonate, and the residue is washed by ethyl acetate. The ILs are obtained by centrifugalization. Subsequently, the catalyst is dried under vacuum to be used in next return. The results are shown in Fig. 6. The PC yield almost remains constant after five cycles. There is only a small amount loss of DEPzI suggesting that the DEPzI has good stability and recyclability in the cycloaddition of CO_2 with PO.

3.5 Catalytic activity toward other epoxides

The generality of DEPzI is examined to catalyze the cycloadditon of CO_2 with five epoxides and the corresponding results are summarized in Table 2. DEPzI is an efficient catalyst for most of epoxides (entries 1-4) with the cyclic carbonate yields around 90% under the experimental reaction condition. The lower **5b** yield should be attributed to the higher hindrance of **5a**, which would greatly impede the nucleophilic attack from anion. Even the reaction time is extended to 24 h, the product yield of **5b** is still the lowest in five investigated epoxides. The difficulty to activate **5a** testifies again the importance of anion to promote the reaction. Reactions listed in Table 2 are performed under 120°C, since there is a slight improvement for product yield of DEPzI when the temperature is increased from 120°C (91.2%) to 130°C (94.4%). To obtain a high ratio of performance/cost, the milder temperature 120°C is employed to study other reactions. Moreover, our main goal is to compare the relative product yields for them rather than obtain their optimal product yields.

3.6 Reaction mechanism

To deeply understand the different catalytic activity of various dialkylpyrazolium ILs with different alkyl chain length, the detailed mechanisms are investigated by DFT method involved by the Gaussian 09 program package [32] associated with the non-covalent interactions (NCI) [33,34] and atoms in molecule (AIM) analysis [35].

The coupling reaction of CO_2 with PO follows three steps, i.e., ring-opening of PO, CO_2 insertion, and ring-closure to generate PC (See Scheme 2). The ring-opening of PO is the synergetic result of both electrophilic attack from cation and nucleophilic attack from anion. The different catalytic activity is aroused by the different

electrophilic attack of cation since they have same anions. In the following calculations, the Γ anion is replaced by Br⁻ anion to save the computational cost. Not only the mechanism but also the relative sequence of catalytic activity would not be varied. The structures of reactants, intermediates, and transition states are optimized by the B3PW91 [36,37] method combined with 6-31G(d,p) [38] basis set. The energies are refined at the M06/6-311+G(2d,2p) level [38,39] on the basis of optimized geometries. The solvent effect is taken into consideration by the polarized continuum model (PCM) in ethyl ether (Et₂O) solvent [40,41]. The atomic charge of some transition states is calculated by natural bond orbital (NBO) analysis [42,43].

Normally, the electrophilic attack is completed by one or several hydrogen atoms in cation. Three possible reaction routes (routes 1-3) are explored to confirm the optimal route, in which each hydrogen atom is taken as the possible electrophile, respectively. The corresponding barrier heights of ring-opening step are shown in Table S2 along with the schematic structures of transition states. The catalytic activity would be further increased if more hydrogen atoms are included in the electrophilic attack. Other three possible routes (routes 4-6) are considered (See Table S2), in which two hydrogen atoms are taken as the electrophile. Owing to the steric hindrance, no more hydrogen atoms from one IL would be employed to activate the O atom of PO. Route 5 is the most possible reaction mechanism because of its lowest barrier heights. Following in the same model, reaction mechanism of other ILs is also confirmed. As shown in Table S3, the ring-opening step is the rate-determining step with the higher barrier height for all studied ILs. In the next discussion, only the barrier height of ring-opening step is mentioned.

The rate-determining barrier height of route A is the lowest suggesting the best catalytic activity for DEPzBr. There is an increase for rate-determining barrier height of route B, which is consistent with the decreased product yield in the presence of DPPzBr. The variation of barrier heights from route B to route D is as small as 0.15 kcal/mol indicating the slightly difference of catalytic activity for DPPzBr, DBPzBr, and DAmPzBr, which is consistent with the experimental sequence. Further extending the alkyl chain length results in relatively little improvement of barrier heights, which is in agreement with their decreased product yield. However, a slightly decreased barrier height is observed for DDoPzBr corresponding to the slight increase of product yield. In general, the sequence of calculated rate-determining barrier heights is totally consistent with the measured experimental product yields. The DEPzBr,

DPPzBr, and DHPzBr are three critical turning points in variation of catalytic activity. The potential energy profiles are shown in Fig. 7 along with the schematic structures of transition states.

Their AIM analysis is also performed to elucidate the role of weak interaction played in the ring-opening step (See Table 3). Two interactions, C-H1...O and C-H2····O, are definitely noncovalent because of the positive Laplacian values of the electron density ($\nabla^2 \rho$). Moreover, C-H2···O interaction is stronger than C-H1···O interaction due to the larger ρ values. Actually, C-H2···O interaction has both covalent and hydrogen bond characteristics since the ρ value of C-H2···O is larger than the upper limitation for classical hydrogen bond (0.035 a.u.). [44,45] Not only C-H1···O interaction but also C-H2···O interaction in TSB1 are smaller than those corresponding values in TSA1 indicating the slightly smaller electrophilic attack of former. While C···Br interaction is almost the same in TSA1 and TSB1 with the ρ values of 0.03400 a.u. and 0.03402 a.u., respectively, suggesting the similar nucleophilic attack for them. The larger electrophilic ability associated with the almost equivalent nucleophilic ability finally results in the lower barrier height for TSA1. As compared with TSA1, TSE1 has the smaller C-H1...O interaction and larger C-H2····O interaction, which is difficult to make a decision between them. Moreover, the C…Br interaction in TSE1 is much larger than that in TSA1, which is favorable to reducing the barrier height. However, the barrier height of TSE1 is higher than that of TSA1. The contrary result should be attributed that the noncovalent interaction is not the sole critical factor to determine the catalytic activity. The electrostatic interaction should also be considered. The natural bond orbital (NBO) of both TSA1 and TSE1 is calculated at the same level (See Fig. S1). TSE1 has not only smaller positive charge for H1 atom but also less negative charge for Br⁻ anion indicating the weaker electrostatic interaction between DHPzBr and PO, which results in its higher barrier height. However, the difference of various routes is not much large since no one has absolute superiority with all favorable items. The corresponding non-covalent interactions (NCI) plots are presented in Fig. 8 to display the non-covalent interaction more clearly.

To investigate the hydrogen bond interaction between reactive hydrogen atom of pyrazolium cation and PO, FT-IR and ¹H NMR analysis of DEPzI with and without

PO is performed. In the FT-IR spectra (Fig. 9), a new characteristic absorbance appears in curve b at 3281 cm⁻¹ due to the stretching vibrations of OH groups indicating the formation of C-O···H bond. Analogous research is also reported by Dai et al [46]. In the ¹H NMR spectra of mixture of DEPzI and PO (Fig. 10), the signal at $\delta = 8.56$ ppm assigned to the C3/C5 proton of pyrazole ring shifts to $\delta = 8.59$ ppm. Additionally, the signal for N-CH₂ proton of DEPzI shifts from $\delta = 4.48$ ppm to $\delta =$ 4.55 ppm suggesting the formation of hydrogen bond between DEPzI and PO. The above analysis indicates that both C3/C5-H and methylene-H can form hydrogen bonds with oxygen atom of PO, which is favorable for ring-opening of PO [47]. Both the FT-IR and ¹H NMR analysis supports the results obtained by DFT calculation and NCI analysis.

4 Conclusions

Dialkylpyrazolium ILs are firstly employed as single-component catalysts for the conversion of CO_2 with PO to produce PC with metal- and solvent-free. Moreover, they would be synthesized by simple and high efficient one-pot method via alkylation reaction. Among the investigated ILs, DEPzI presents the best catalytic activity with the highest product yield. When the alkyl chain in cation is increased, the catalytic activity is decreased with step-shaped character. The optimal reaction condition is confirmed to be 130°C, 2 MPa initial CO₂ pressure and 4 h with 1 mol% DEPzI loading. Moreover, DEPzI could be reused for five cycles without obvious loss of catalytic activity. Finally, the detailed mechanism investigated by DFT associated with NCI and AIM analysis shows that the ring-opening of PO is promoted by both the hydrogen bond and electrostatic interaction. The dialkylpyrazolium ILs are potential candidates in the CO₂ fixation with prominent advantages including facile synthesis, good recyclability, and acceptable catalytic activity, which is an important topic for sustainable development.

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Fig. 1 TGA traces for five selected ILs.

Fig. 1 TGA traces for five selected ILs.



Fig. 2 Influence of catalyst loading on PC yield and selectivity (reaction condition: PO 0.1 mol, initial CO₂ pressure 2 MPa, 130 $^{\circ}$ C, 4 h).



Fig. 3 Influence of CO₂ pressure on PC yield and selectivity (reaction condition: PO 0.1 mol, DEPzI 1 mol%, 130 °C, 4 h).



Fig. 4 Influence of temperature on PC yield and selectivity (reaction condition: PO 0.1 mol, DEPzI 1 mol%, initial CO₂ pressure 2 MPa, 4 h).



Fig. 5 Influence of reaction time on PC yield and selectivity (reaction condition: PO 0.1 mol, DEPzI 1 mol%, initial CO₂ pressure 2 MPa, 130 °C).



Fig. 6 Reused performance of the catalyst (Reaction condition: PO 0.1 mol, DEPzI 1 mol%, initial CO₂ pressure 2 MPa,130 °C, 4 h).



Fig. 7 Energy profiles for the cycloaddition reaction along route A, route B, and route E calculated at the M06/6-311+G(2d, 2p)//B3PW91/6-31G(d, p) (PCM) level in Et_2O solvent.





Fig. 8 NCI plots for **TSA1**, **TSB1**, and **TSE1**. The corresponding 3D plots are displayed below with blue regions representing strong electrostatic interactions and green regions.



Fig. 9 FT-IR spectra of DEPzI (a) without and (b) with PO.



Fig. 10 ¹H NMR spectra ($[D_6]DMSO$, 25°C) of DEPzI (0.1 mmol) with and without PO (0.2 mmol).



$$\begin{split} \mathbf{R} = \mathbf{C}\mathbf{H}_3, \, \mathbf{C}_2\mathbf{H}_5, \, \textit{n-C}_3\mathbf{H}_7, \, \textit{n-C}_4\mathbf{H}_9, \, \textit{n-C}_5\mathbf{H}_{11}, \, \textit{n-C}_6\mathbf{H}_{13}, \, \textit{n-C}_8\mathbf{H}_{17}, \, \textit{n-C}_{10}\mathbf{H}_{21}, \, \textit{n-C}_{12}\mathbf{H}_{25}; \\ \mathbf{X} = \mathbf{Br}, \, \mathbf{I}; \, \mathbf{Y} = \mathbf{B}\mathbf{F}_4, \, \mathbf{P}\mathbf{F}_6 \end{split}$$



Scheme 1 Synthetic route and structures of the dialkylpyrazolium ionic liquids (DAPzILs).



Scheme 2 The proposed mechanism of route A.

Entry	Catalysts	Time/h	Yield ^b /%
1	None	8	-
2	KBr	8	3.3
3	DMPzI	4	83.3
4	DEPzI	4	91.2(96.1) ^c
5	DPPzI	4	89.1
6	DBPzI	4	89.1
7	DAmPzI	4	89.9
8	DEPzBr	4	89.1(94.2) ^c
9	DPPzBr	4	87.4
10	DBPzBr	4	87.9
11	DAmPzBr	4	87.4
12	DHPzBr	4	80.3
13	DOPzBr	4	79.1
14	DDePzBr	4	73.9
15	DDoPzBr	4	78.1
16	DEPzBF ₄	4	51.2
17	DEPzPF ₆	4	5.5

 Table 1 Catalytic performance of various catalysts ^a

^{*a*}Reaction conditions: PO 0.1 mol, catalyst 1 mol% (mol% of catalyst moieties to epoxide), 120 °C, initial CO₂ pressure 2 MPa. ^{*b*}Isolated yield. ^{*c*}Yield was determined by GC.

Entry	Epoxide	Cyclic carbonate	Yield ^b /%
1	∠0 1a	o l b	88.1
2		o 2b	91.2
3		o o c l 3b	86.8
4	م 4a	o 4b	90.4
5	o 5a	o 5b	60.2 ^c

Table 2 Cycloaddition of CO₂ with various epoxides catalyzed by DEPzI^a.

^{*a*}Reaction conditions: epoxide 0.1 mol, DEPzI 1 mol% (mol% of pyrazolium salt moieties to epoxide), 2 MPa CO₂, 120 °C, 4 h. ^{*b*}Isolated yield. ^{*c*}Reaction time: 24 h.

Transition state	X-YZ	${ m Sign}(\lambda_2) ho$	ρ	$ abla^2 ho$
TSA1	С-Н1…О	-0.02192	0.02192	0.06477
	С-Н2…О	-0.03984	0.03984	0.11484
	C…Br	-0.03400	0.03400	0.06887
TSB1	С-Н1…О	-0.02139	0.02139	0.06365
	С-Н2…О	-0.03926	0.03926	0.11182
	C…Br	-0.03402	0.03402	0.06870
TSE1	С-Н1…О	-0.01863	0.01863	0.05394
	С-Н2…О	-0.04052	0.04052	0.11969
	C····Br	-0.04065	0.04065	0.07152

Table 3 Selected topological parameters of the bond critical point in the most stabletransition state calculated at the B3PW91/6-31G(d, p) level of theory.