

# Protic ionic liquids: A highly efficient catalyst for synthesis of cyclic carbonate from carbon dioxide and epoxides

Linfei Xiao, Dan Su, Chengtao Yue, Wei Wu\*

Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, PR China

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## ABSTRACT

An efficient, inexpensive, easily prepared and sustainable catalytic system of protic ionic liquids was developed for cycloaddition of CO<sub>2</sub> and epoxides to produce cyclic carbonates without using any co-catalyst and organic solvent. The effects of the acidity and structure of protic ionic liquid on the catalytic performance were investigated and the various reaction conditions were optimized. Notably, this catalyst was used for five times at least without appreciable loss of catalytic activity and applied for various epoxide for synthesis of corresponding cyclic carbonate in high selectivity and yield. Additionally, a mechanism for the synergistic effects of cation and anion in protic ionic liquids was also proposed.

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## 1. Introduction

Chemical fixation of CO<sub>2</sub> and its use as an inexpensive, nontoxic, highly abundant, C1 building block are great current interest due to the growing concern about the deleterious effects of greenhouse gases on our environment [1–3]. One of the most promising ways for effective utilization of CO<sub>2</sub> is the synthesis of five-membered cyclic carbonates via coupling carbon dioxide and epoxides. Cyclic carbonates are valuable industrial raw materials, which are useful as aprotic polar solvents, electrolytes in lithium secondary batteries, intermediates for the pharmaceutical and fine chemical industries, and precursors for synthesizing polycarbonate materials [4,5].

In the past few decades, the numerous heterogeneous and homogeneous catalysts have been developed for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> [6–8]. Such as metal oxides [9], molecular sieves [10], ion-exchange resins [11], nanoparticles [12], alkali metal salts [13], quaternary ammonium salts [14–16], transition metal complexes [4,17–20], metal-organic frameworks [21], N-heterocyclic carbenes [22], Lewis acids or bases [23,24], ionic liquid [25–29], and so on. Among these catalysts, ionic liquids have been shown excellent activity in the synthesis of cyclic carbonates from carbon dioxide and epoxides. However, the inherent disadvantage of ionic liquids is the requirement for high CO<sub>2</sub> pressure or transition metal additives

[30,31]. Therefore, the development of a low cost, easily prepared, thermal stable and efficient single component catalyst for the conversion of CO<sub>2</sub> to cyclic carbonate is still an important task.

Recently, Shi et al. found that hydrogen bond can accelerate rate of cycloaddition of epoxides with CO<sub>2</sub> when the NaI/PPh<sub>3</sub>/PhOH was used as a catalyst system [32], the similar results was founded when the hydroxyl or carboxylic groups functionalized imidazolium based ionic liquids was used as a catalyst for synthesizing cyclic carbonate from carbon dioxide and epoxide [33,34]. In context, we conceived that the protic ionic liquids have a great potential to accelerate the reaction in forward direction, due to its strong chelating ability through hydrogen bond with oxygen atom of epoxide enabling the ring opening [35]. Protic ionic liquids are an important subgroup of ionic liquids formed by a combination of equimolar amounts of a Brønsted acid and a Brønsted base [36–38]. In contrast to other ionic liquids, protic ionic liquids have a number of unique properties, just as low cost, easy preparation and a variable proton activity [39]. The key property that distinguishes protic ionic liquids from other ionic liquids is the proton transfer from the acid to the base, leading to the presence of proton-donor and proton-acceptor sites, which can be used to build a hydrogen-bond network [40]. The number of H-bond donors, the interaction strength, and the network formation can be varied as desired. Until now, protic ionic liquids was used widely in organic reaction as solvent or catalyst [41–43].

In the present work, a serious of imidazolium based protic ionic liquids was synthesized, characterized and employed as catalysts for coupling reaction of epoxide and CO<sub>2</sub> to form five-membered cyclic carbonate without using transition metal additives and

\* Corresponding author. Tel.: +86 451 86609227; fax: +86 451 86609227.  
E-mail address: [wuwei@hlju.edu.cn](mailto:wuwei@hlju.edu.cn) (W. Wu).

co-solvent. Under the optimized reaction conditions, protic ionic liquids exhibited significant activity providing good to excellent yield of desired product with appreciable recyclability for five consecutive recycles and a possible mechanism was proposed.

## 2. Experimental

Propylene oxide was produced by Sinopharm Chemical Reagent Co. Ltd., glycidyl phenyl ether, epichlorohydrin, styrene oxide, cyclohexene oxide were purchased from Aldrich Chemical Co. Ltd., The CO<sub>2</sub> (99.99%) was obtained from Qinghua Gas Co. Ltd. The other organic compounds were purchased from commercial market and used without further purification. The <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) were run on a Bruker AV400 spectrometer with TMS as the internal standard. ESI (MS) spectra were measured using an AB Sciex API 3000 spectrometer. The Hammett acidity function of protic ionic liquids was determined with using 4-nitroaniline as the basic indicator by a Shimadzu UV-vis Spectrophotometer UV-3600 (Hammett method). The products, cyclic carbonates, were analyzed by a HP 6890/5973 GC-MS and a gas chromatography (GC, Agilent 6820) equipped with a flame-ionized detector.

### 2.1. Preparation and characterization of protic ionic liquids

The protic ionic liquids were synthesized according to the previous literature. [44]

1-Methylimidazolium bromide ([HMim]Br) was prepared as follows (Scheme 1): an equimolar amount of HBr was added dropwise to 1-methylimidazole, and the mixtures were stirred for 4–5 h at 60 °C to ensure that all of the base was reacted. Then, water was removed under reduced pressure to obtain a protic ionic liquid [HMim]Br.

The synthesis procedure of protic ionic liquids methylimidazolium chloride ([HMim]Cl), 1-methylimidazolium iodide ([HMim]I), 1-ethylimidazolium bromide ([Heim]Br), 1-butylimidazolium bromide ([HBim]Br), imidazolium bromide ([Him]Br), triethylammonium bromide ([HTEA]Br) and pyridinium bromide ([HPy]Br) were similar to that of ionic liquid [HMim]Br (Fig. 1).

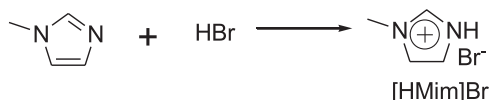
The structures of protic ionic liquids were determined by NMR and ESI-MS, the data of NMR and MS was provided as follows:

[HMim]Cl: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ (ppm) 8.63 (s, 1H, N-CH-N), 7.40 (s, 2H, N-CH-CH-N), 3.89 (s, 3H, N-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ (ppm) 135.0, 123.1, 119.5, 35.7. MS (ESI): *m/z* 83 [M–Cl]<sup>+</sup>.

[HMim]Br: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ (ppm) 8.65 (s, 1H, N-CH-N), 7.75 (s, 2H, N-CH-CH-N), 3.90 (s, 3H, N-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ (ppm) 135.1, 123.1, 119.6, 35.7. MS (ESI): *m/z* 83 [M–Br]<sup>+</sup>.

[HMim]I: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ (ppm) 8.63 (s, 1H, N-CH-N), 7.41 (s, 2H, N-CH-CH-N), 3.89 (s, 3H, N-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ (ppm) 135.1, 123.1, 119.6, 35.9. MS (ESI): *m/z* 83 [M–I]<sup>+</sup>.

[HEim]Br: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 14.88 (s, 1H, NH), 9.62 (s, 1H, N-CH-N), 7.42 (s, 1H, CH-NH), 7.20 (s, 1H, CH-NCH<sub>2</sub>CH<sub>3</sub>), 4.44 (q, *J* = 7.3 Hz, 2H, CH<sub>2</sub>), 1.62 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 133.5, 120.7, 118.9, 44.4, 15.2. MS (ESI): *m/z* 97 [M–Br]<sup>+</sup>.



Scheme 1. Synthesis of protic ionic liquids.

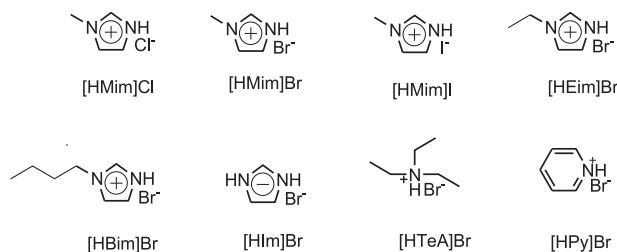


Fig. 1. Protic ionic liquids.

[HBim]Br: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 14.58 (s, 1H, NH), 9.59 (s, 1H, N-CH-N), 7.48 (s, 1H, CH-NCH<sub>2</sub>), 7.34 (s, 1H, CH-NH), 4.42 (t, *J* = 6.0 Hz, 2H, N-CH<sub>2</sub>CH<sub>2</sub>), 1.91 (m, *J* = 7.4 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.39 (m, *J* = 9.3 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 0.97 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ (ppm) 133.7, 120.9, 118.8, 48.8, 31.4, 18.5, 12.6. ESI (MS): *m/z* 125 [M–Br]<sup>+</sup>.

[Him]Br: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ (ppm) 8.66 (s, 1H, N-CH-N), 7.44 (s, 2H, CH-CH). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ (ppm) 133.4, 119.0. MS (ESI): *m/z* 69 [M–Br]<sup>+</sup>.

[HTEA]Br: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 10.90 (s, 1H, NH), 3.18 (m, *J* = 7.2 Hz, 6H, CH<sub>2</sub>), 1.46 (t, *J* = 7.2 Hz, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 45.6, 8.1. MS (ESI): *m/z* 102 [M–Br]<sup>+</sup>.

[HPy]Br: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 9.05 (d, *J* = 5.2 Hz, 2H, HN-CH), 8.60 (m, *J* = 8.0 Hz, 1H, CH-CHCHN), 8.14 (q, *J* = 8.0 Hz, 2H, CH-CHN). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 146.4, 140.3, 127.2. MS (ESI): *m/z* 80 [M–Br]<sup>+</sup>.

### 2.2. Determining the acidic strength of protic ionic liquids

The acidity of protic ionic liquids was determined by the Hammett acidity function (H<sub>0</sub>) with using 4-nitroaniline as the basic indicator [44]. In the present case, this method consists of evaluating the protonation extent of uncharged 4-nitroaniline (named I) in water, in terms of the measurable ratio [I]/[IH<sup>+</sup>]. The maximal absorbance of the unprotonated 4-nitroaniline was observed in water (Fig. 2) and it was decreased in carrying degrees when protic ionic liquid was added into the mixture, respectively. By taking the total unprotonated indicator as the initial reference (ILs were not added to the solution), the [I]/[IH<sup>+</sup>] ratio was determined from the measured absorbance after treating by protic ionic liquid, then the Hammett function (H<sub>0</sub>) of protic ionic liquid was calculated by the equation: H<sub>0</sub> = pK(I)<sub>aq</sub> + log ([I]/[IH<sup>+</sup>]).

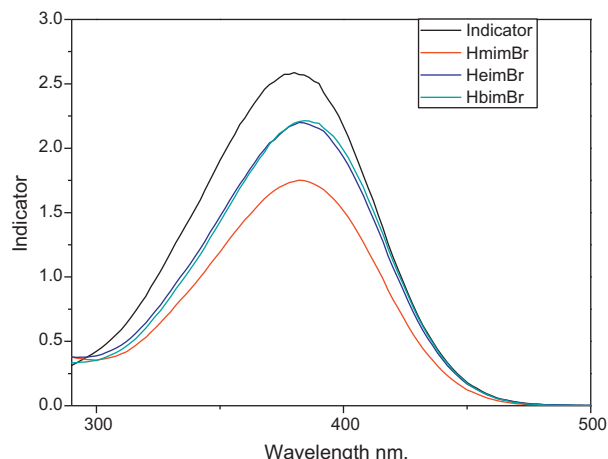


Fig. 2. UV-vis absorption spectra of 4-nitroaniline in water.

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