



Functionalized phosphonium-based ionic liquids as efficient catalysts for the synthesis of cyclic carbonate from epoxides and carbon dioxide

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ABSTRACT

A series of novel functionalized phosphonium-based ionic liquids (FPBILs) were synthesized by a simple method, and first evaluated as catalysts for the synthesis of cyclic carbonates through the cycloaddition of CO₂ to epoxides in the absence of co-catalyst and solvent. The FPBILs perform well in the cycloaddition reaction, especially the carboxyl-functionalized one. Over [Ph₃PC₂H₄COOH]Br, the yield of propylene carbonate is 97.3% (TOF = 64.9 h⁻¹) at 130 °C and 2.5 MPa in 3 h. The synergistic effects of polarization induced by hydrogen bonding and nucleophilic attack of Br⁻ anion account for the excellent performance. Furthermore, the FPBILs with moderate methylene chain length show superior catalytic activity. It is because they have both strong acidity and weak electrostatic interaction between phosphonium cation and halide anion. The strong acidity facilitates the ring-opening of epoxy, and the weak electrostatic interaction enhances the nucleophilic attack capability of Br⁻. It is envisaged that the metal- and solvent-free process has high potential for the catalytic conversion of CO₂ into value-added chemicals.

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1. Introduction

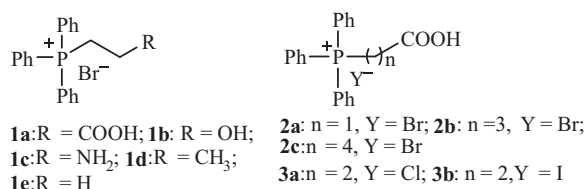
With the fast consumption of fossil fuels, “C1 resource crisis” has become a concern [1]. Despite blamed for global warming, CO₂ is a C1 resource that is renewable, nontoxic, abundant, and inexpensive [2–4]. The fixation of CO₂ to generate valuable chemicals such as cyclic carbonates is meaningful. Cyclic carbonates are used as polar aprotic solvents, as electrolytes in lithium secondary batteries, as precursors for the formation of polycarbonates, and as intermediates in the production of pharmaceuticals and fine chemicals [2–4].

A wide range of catalysts have been explored for the synthesis of cyclic carbonates, including metal oxides [5,6], modified molecular sieves [7,8], alkali metal salts [9], organometallic complexes [10,11], and ionic liquids (ILs) [12–30]. Since the 2000s, the use of ILs has attracted much interest, such as imidazolium salts [12–19], quaternary ammonium salts [18,20,21], quaternary phosphonium salts [22,23], pyridinium salts [25], guanidinium salts [26–28], and other type ILs [29,30] were tested as catalysts for the cycloaddition of CO₂ into epoxides. The ILs show favorable features such as good solvating ability, negligible vapor pressure, and variable polarity but most of them suffer from shortcomings such as

unsatisfactory activity, harsh reaction conditions, being water- or air-sensitive, and the need of a metal salt as co-catalyst. Unlike imidazolium-based ILs, phosphonium-based ILs has not been well studied because of such shortcomings. For example, He et al. [22] used polyfluoroalkyl phosphonium iodides as catalyst for the synthesis of propylene carbonate (PC) from propylene oxide (PO) and CO₂. Although the catalysts can be separated from the PC product, the harsh reaction conditions (14.0 MPa, 24 h) seriously limit their application. Sun et al. [23] reported that in the presence of ZnCl₂, traditional quaternary phosphonium halide exhibits good catalytic activity. Our group also reported a ZnBr₂–Ph₄PI system that shows excellent catalytic performance [24], but zinc halide is needed as a co-catalyst. Although the catalyst systems mentioned above exhibit good activity using metal halide as co-catalyst, the quaternary phosphonium ionic liquids (such as PPh₃BuBr, PPh₃BuCl, PPh₃BuI, PPh₃EtBr, PPh₃PrBr, and PPh₃HeBr) are themselves low in activity [31]. Despite the presence of water could remarkably improve the activity of quaternary phosphonium ionic liquids, problems such as low PC selectivity (<95%) and difficulty in product separation exist [31]. Hence, it is highly desirable to develop one-component phosphonium-based ILs as effective catalysts for commercial synthesis of cyclic carbonates.

Recently, it was demonstrated that by introducing certain functional groups into the cation and/or anion of traditional ILs, the “tailor-made” materials are task-specific in diverse areas [32–36].

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Scheme 1. Structures of FPBILs.

For the synthesis of cyclic carbonates by cycloaddition of CO₂ to epoxides, imidazolium-based ILs that contain hydroxyl [18,37] or carboxyl [19,38,39] group show better catalytic performance than traditional ILs. To the best of our knowledge, there is no application of functionalized phosphonium-based ILs (FPBILs) for the synthesis of cyclic carbonates. Herein, we report the synthesis of a series of phosphonium-based ILs that are functionalized with hydroxyl, carboxyl, and amino groups (Scheme 1). For the first time, these novel materials were tested as catalysts for the synthesis of cyclic carbonates through cycloaddition of CO₂ to epoxides. The FPBILs display high epoxide conversion, and with excellent selectivity show almost quantitative yield of cyclic carbonates in the absence of solvent or co-catalyst. In the study, the effect of catalyst structure and reaction parameters on performance was investigated in detail.

2. Experimental

2.1. Chemicals

Propylene oxide was purchased from Sinopharm Chemical Reagent Co., Ltd. Other epoxides were purchased from Alfa Aesar China Co., Ltd. Triphenylphosphine (Ph₃P), 2-bromoethanol, 2-bromoethylamine hydrobromide, bromoethane, 3-bromopropane, 3-bromopropionic acid, 3-chloropropionic acid, 3-iodopropanoic acid, 4-bromobutyric acid, and 5-bromovaleric acid were purchased from Shanghai Jingchun Industry Co., Ltd. All chemicals were used as received. The CO₂ (99.9% purity) purchased from Nanchang Guoteng Gas Co. was used without any further treatment.

2.2. Synthesis of phosphonium-based ionic liquids

A typical procedure for the preparation of [Ph₃PC₂H₄NH₂]⁺Br⁻ (**1c**) is as follows: A solution of triphenylphosphine (5 mmol) and 2-bromoethylamine hydrobromide (5 mmol) in 20 mL toluene was heated and subject to reflux for 24 h. After cooling, the resulted crude solid was filtered out, and stirred in 10 mL triethylamine for 4 h. Afterward, the triethylamine was removed, and the as-obtained solid was washed three times with ethyl acetate, then dried at 60 °C under vacuum for 12 h to give product **1c** in the form of a pale yellow solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.95–7.76 (m, 15H), 3.68 (t, *J* = 6.0 Hz, 2H), 3.48–3.42 (m, 2H). IR (neat): *n* = 3396, 3053, 3026, 2976, 2973, 2894, 1583, 1486, 1433, 805, 802, 724, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 386.0677, calcd. for C₂₀H₂₂NPBr (M + H): 386.0673.

Other FPBILs were prepared likewise but without the procedure of stirring in triethylamine.

[Ph₃PC₂H₄COOH]⁺Br⁻ (**1a**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.77 (s, 1H), 7.90–7.11 (m, 15H), 3.85–3.77 (m, 2H), 2.61–2.54 (m, 2H). IR (neat): *n* = 3055, 3020, 2937, 2896, 2883, 1725, 1585, 1485, 1436, 724, 692 cm⁻¹. HR-MS (QTOF): *m/z* = 415.0473, calcd. for C₂₁H₂₁O₂PBr (M + H): 415.0463.

[Ph₃PC₂H₄OH]⁺Br⁻ (**1b**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.93–7.75 (m, 15H), 3.59–3.51 (m, 2H), 1.69–1.65 (m, 2H). IR (neat): *n* = 3317, 3053, 3026, 2976, 2937, 2894, 1583, 1486, 1433,

805, 802, 742, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 387.0508, calcd. for C₂₀H₂₁OPBr (M + H): 387.0513.

[Ph₃PC₃H₇]⁺Br⁻ (**1d**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.00–7.70 (m, 15H), 3.69–3.61 (m, 2H), 1.68–1.59 (m, 2H), 1.17–1.13 (m, 3H). IR (neat): *n* = 3076, 3051, 2925, 2885, 2879, 1585, 1485, 1436, 1380, 746, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 385.0718, calcd. for C₂₁H₂₃PBr (M + H): 385.0721.

[Ph₃PC₂H₅]⁺Br⁻ (**1e**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.97–7.79 (m, 15H), 3.67–3.59 (m, 2H), 1.30–1.21 (m, 3H). IR (neat): *n* = 3072, 3045, 2923, 2883, 2876, 1585, 1485, 1436, 1379, 737, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 371.0552, calcd. for C₂₀H₂₁PBr (M + H): 371.0564.

[Ph₃PCH₂COOH]⁺Br⁻ (**2a**): Brown solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.72 (s, 1H), 7.81–7.34 (m, 15H), 3.69 (s, 2H). IR (neat): *n* = 3055, 3010, 2937, 2891, 2881, 1716, 1585, 1485, 1436, 742, 692 cm⁻¹. HR-MS (QTOF): *m/z* = 401.0306, calcd. for C₂₀H₁₉O₂PBr (M + H): 401.0306.

[Ph₃PC₃H₆COOH]⁺Br⁻ (**2b**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.42 (s, 1H), 8.06–7.77 (m, 15H), 3.79–3.72 (m, 2H), 2.48–2.46 (m, 2H), 1.75–1.69 (m, 2H). IR (neat): *n* = 3057, 3026, 2947, 2898, 2878, 1727, 1587, 1486, 1433, 738, 686 cm⁻¹. HR-MS (QTOF): *m/z* = 429.0623, calcd. for C₂₂H₂₃O₂PBr (M + H): 429.0619.

[Ph₃PC₄H₈COOH]⁺Br⁻ (**2c**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.75 (s, 1H), 7.93–7.75 (m, 15H), 3.85–3.77 (m, 2H), 3.44–3.35 (m, 2H), 2.93–2.86 (m, 2H), 2.61–2.50 (m, 2H). IR (neat): *n* = 3062, 3028, 2960, 2904, 2873, 1726, 1583, 1484, 1436, 742, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 443.0762, calcd. for C₂₃H₂₅O₂PBr (M + H): 443.0775.

[Ph₃PC₂H₄COOH]⁺Cl⁻ (**3a**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.77 (s, 1H), 7.93–7.62 (m, 15H), 3.83–3.76 (m, 2H), 2.60–2.56 (m, 2H). IR (neat): *n* = 3052, 3010, 2989, 2939, 2893, 1739, 1583, 1485, 1436, 740, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 371.0968, calcd. for C₂₁H₂₁O₂PCl (M + H): 371.0968.

[Ph₃PC₂H₄COOH]⁺I⁻ (**3b**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.77 (s, 1H), 7.93–7.77 (m, 15H), 3.84–3.76 (m, 2H), 2.60–2.56 (m, 2H). IR (neat): *n* = 3059, 3028, 2958, 2896, 2875, 1725, 1583, 1484, 1433, 740, 690 cm⁻¹. HR-MS (QTOF): *m/z* = 463.0332, calcd. for C₂₁H₂₁O₂PI (M + H): 463.0324.

2.3. Synthesis of cyclic carbonates

The cycloaddition reactions were conducted in a 50 mL high-pressure stainless-steel autoclave equipped with a magnetic stirring bar. In a typical run, the reactor was charged with epoxide (35.7 mmol), catalyst (0.5 mol%, calculated according to the amount of ionic liquid), and an appropriate amount of biphenyl (as internal standard for GC analysis). After the reactor was fed with CO₂ to a desired pressure, the autoclave with its contents was heated to a selected temperature and stirred for a designated period of time. Then the reactor was cooled to 0 °C in an ice-water bath, and the remaining CO₂ was released. The resulting mixture was analyzed using a GC-mass spectrometer. The products were quantitatively 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).

3. Results and discussion

3.1. Catalytic performance

The synthesis of PC through the cycloaddition of CO₂ to PO was chosen as model reaction to evaluate the catalytic activity of the as-synthesized FPBILs, and the results are summarized in Table 1. It can be seen that Ph₃P and 3-bromopropionic acid show poor catalytic activity when used alone (entries 1, 2), whereas the as-synthesized

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