



# Highly efficient and selective synthesis of dibutyl carbonate via the synergistic dual activation catalysis of tetraethylammonium proline ionic liquids

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## ABSTRACT

A facile, highly efficient and phosgene-free synthesis process of dimethyl carbonate (DMC) with *n*-butanol (BuOH) to dibutyl carbonate (DBC) by transesterification reaction has been studied in detail using tetraethylammonium-based amino acid ionic liquids ([N<sub>2222</sub>][AA]) as homogeneous catalysts. The results indicated that tetraethylammonium proline ([N<sub>2222</sub>][Pro]) exhibited the best catalytic activity in compared to other four [N<sub>2222</sub>][AA], and DBC could be obtained at a yield of 72% under optimum conditions. Furthermore, quantum-mechanical calculations manifested that such high DBC yield originated from the synergistic dual activation catalysis of [N<sub>2222</sub>][Pro]. [N<sub>2222</sub>][Pro] could activate BuOH and DMC well at the same time, which enhances the electrophilicity of BuOH and the nucleophilicity of DMC respectively, leading to the excellence catalytic performance.

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## 1. Introduction

Dibutyl carbonate (DBC) is an important long-chain alkyl carbonate in petrochemical industry, and it is extensively used for the production of various organic and polymeric materials, particularly for the synthesis of polycarbonate [1–5]. DBC is also considered to be an excellent environmental protection lubricant base material because of its good lubricity and wearability, corrosion resistance, high thermal oxidative stability, and outstanding solubility [1–4]. The synthesis of DBC therefore has been growing fast in the past years due to a continual demand.

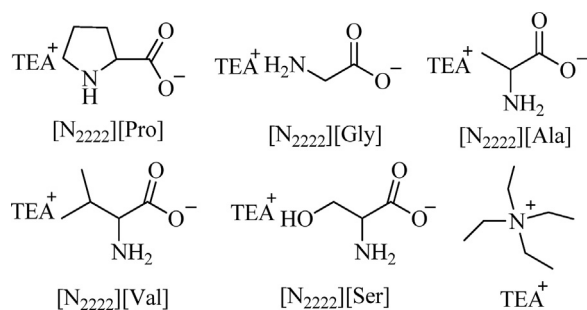
Traditionally, DBC has been produced by the reaction of phosgene with *n*-butanol (BuOH). However, this phosgenation technology has several serious inherent drawbacks, including the use of highly toxic phosgene, the corrosion of metal equipment, and a large amount of by-product hydrogen chloride. Consequently, the phosgene-free synthesis of DBC with a more environmentally friendly process continues to be appealing [6,7]. Recently, the transesterification of dimethyl carbonate (DMC) with BuOH has attracted much attention as the alternative route for the production of DBC, with the advantages of low pollution and corrosion,

green raw material, and mild reaction conditions [8,9]. Generally, this transesterification route can be described as a two-step process, which involves the first step of the transesterification of DMC with BuOH to form methyl butyl carbonate (MBC) (Eq. (1)) and the second step of the transesterification of MBC with BuOH to produce DBC (Eq. (2)).



At present, there are already several literatures on the synthesis of long-chain alkyl carbonate (such as diethyl carbonate, dipropyl carbonate, dibutyl carbonate, dipentyl carbonate, and diphenyl carbonate) through transesterification reaction. For example, Murugan and Bajaj [10] studied the synthesis of diethyl carbonate using KF/Al<sub>2</sub>O<sub>3</sub> as catalyst and the yield of diethyl carbonate could reach 61.6%. Ma and co-worker [11] reported the synthesis of dipropyl carbonate with a yield of 70% using Mg–Al composite oxide containing La as efficient and reusable catalyst. Shaikh and Sivaram [12] reported that the transesterification of DMC with BuOH could obtain the DBC yield of 72% at 12 h in the presence of *n*-Bu<sub>2</sub>SnO as catalyst. Tang et al. [13] had further investigated the transesterification of DMC with phenol catalyzed by core-shell TiO<sub>2</sub>@SiO<sub>2</sub> the yield of diphenyl carbonate was only 24.1% at 9 h. Although these investigations have made strides, these results are not entirely satisfactory because of low reaction selectivity and

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**Scheme 1.** Structures of five  $[N_{2222}][AA]$  ILs.

product yield, harsh reaction conditions, high mass transfer resistance, and easy deactivation of catalysts. There remains a strong need to develop novel catalyst materials with high efficiency and selectivity for the synthesis of long-chain alkyl carbonate, especially for DBC.

In recent years, ionic liquids (ILs), as new type of green solvent and efficient catalyst, have been received much attention in industrial and academic area. They present a broad application prospect and have been successfully introduced into the field of catalysis owing to their unique chemical properties such as negligible vapor pressure, structural variety, excellent thermal stability, and remarkable solubility [14–17]. To date, ILs have been extensively used in alkylation, esterification, transesterification, acetalization, and so on [18–22], which obviously exhibits high catalytic activity and selectivity. However, to the best of our knowledge, there has been no mention of using ILs as catalysts for the synthesis of DBC. Moreover, most studies have only focused on the catalytic performance of various ILs. The key investigation on the relationship between the structural geometry of ILs and their catalytic performance to study the intrinsic reaction mechanism is still scarce in the literatures. Hence, we believe that there is a need to investigate the activation mechanism of ILs for the highly efficient synthesis of DBC, and these results will be applicable to explore the possibility of IL-based industrial processes and to provide optimal parameters.

Therefore, a series of tetraethylammonium-based amino acid ionic liquid ( $[N_{2222}][AA]$ ) had been prepared and their catalytic activities for the synthesis of DBC were investigated in this work. The reaction parameters such as reaction time, temperature, catalyst loading, and molar ratio of reactants were explored in detail to obtain the optimum conditions. Furthermore, the effect of structural geometry of ILs on their catalytic activity was studied and a plausible reaction mechanism involved the synergistic dual activation catalysis of  $[N_{2222}][AA]$  was then proposed.

## 2. Experimental

### 2.1. Chemicals and catalyst preparations

Tetraethylammonium hydroxide pentahydrate (purity  $\geq 99\%$ ), and tetraethylammonium hydroxide (25 wt% aqueous solution) were purchased from Aldrich Chemical Reagent Co. Ltd. Other reagents such as DMC, amino acid, alcohol, triethyl amine, potassium carbonate, and sodium hydroxide were of analytical grade and used without any further purification.

Five  $[N_{2222}][AA]$  ILs (as shown in Scheme 1) were synthesized via the simple neutralization reactions as follows. Slightly excess amount of amino acid (glycine, valine, alanine, serine and proline) was added to  $[N_{2222}][OH]$  aqueous solution. The mixture was then stirred at room temperature for 2 h. Subsequently, water was distilled off at  $60^\circ\text{C}$  under reduced pressure. The reaction mixture was added into ethanol, and filtrated to remove excess amino acid. Filtrate was evaporated to remove solvents. The product  $[N_{2222}][AA]$

ILs thus obtained were dried in high vacuum for 12 h at  $90^\circ\text{C}$ . The structures of these  $[N_{2222}][AA]$  ILs were confirmed by  $^1\text{H}$  NMR, elemental analysis and FT-IR spectroscopy, and no impurities were found by  $^1\text{H}$  NMR. All the detailed characterization results were given in supplementary data.

### 2.2. Reaction procedures

In a typical procedure,  $[N_{2222}][Pro]$  (0.5 wt%, based on the total weight of DMC and BuOH), DMC (20 mmol) and BuOH (80 mmol) were added into a round-bottomed flask (50 mL) fitted with a magnetic stirrer and condenser. Then, the reaction mixture was vigorously stirred and allowed to proceed for 1–6 h with the heating at the designed temperature (e.g.,  $110^\circ\text{C}$ ). After the reaction was completed, the reactor was cooled down. About 0.2 mL of liquid sample was taken from the reactor and detected by gas chromatography (GC). Subsequently, the reaction mixture was extracted with deionized water ( $10\text{ mL} \times 3$ ), and the system thus forms a liquid–liquid biphasic, and the aqueous phase containing ILs could be easily separated by simple decantation. After that, the catalyst ILs were further in a vacuum oven at  $80^\circ\text{C}$  for 12 h to remove water and the residual reactants prior to reuse in the next run. Qualitative analyses of products were examined by a Thermo Trace 1300 GC-ISQ, and quantitative analyses were carried out by a GC-FID (Agilent 7890B). The detailed analysis conditions were described as follows: the injector and detector temperatures were 250 and  $250^\circ\text{C}$ , respectively; the column temperature was increased stepwise to  $200^\circ\text{C}$ , holding at  $80^\circ\text{C}$  for 2 min, increasing to  $200^\circ\text{C}$  at  $40^\circ\text{C min}^{-1}$ , holding at  $200^\circ\text{C}$  for 5 min. Then the conversion and selectivity were calculated according to the area of chromatograph peak using biphenyl as an internal standard.

### 2.3. Definition of DMC conversion, DBC selectivity and DBC yield

Qualitative analysis of GC–MS confirmed that DMC reacted to give DBC and MBC as the unique products and no other products were detected in the reaction. Thus the conversion of DMC is defined as the ratio of the number of moles of DBC and MBC production in the reaction to the total number of moles of DMC initially added. The selectivity for DBC is defined as the ratio of the number of moles of DBC to the number of moles of DBC and MBC. The date of DMC conversion multiply by DBC selectivity was the DBC yield.

$$\text{DMC conversion} = \frac{\text{moles of (DBC + MBC) produced}}{\text{moles of DMC initially added}}$$

$$\text{DBC selectivity} = \frac{\text{mol (DBC)}}{\text{mol (DBC) + mol (MBC)}}$$

### 2.4. Computational methods

Density functional theory (DFT) was employed to perform the geometry optimizations and natural bond orbital (NBO) charge analysis at the B3LYP/6-31++G(d,p) level using the Gaussian 09 program package [23]. Each final optimized structure of  $[N_{2222}][AA]$ , DMC, BuOH and their complexes was checked to be a true minimum through frequency calculation at the corresponding levels.

## 3. Results and discussion

### 3.1. Catalytic activities of different catalysts

Five  $[N_{2222}][AA]$  ILs were employed as catalysts to test their catalytic activities in the transesterification reaction of DMC with BuOH, and the results are summarized

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