



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 ([N₂₂₂₂][AA]) as homogeneous catalysts. The results indicated that tetraethylammonium proline ([N₂₂₂₂][Pro]) exhibited the best catalytic activity in compared to other four [N₂₂₂₂][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 [N₂₂₂₂][Pro]. [N₂₂₂₂][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,

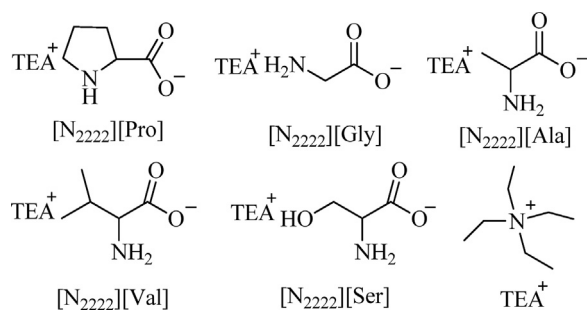
green raw material, and mild reaction conditions [8,9]. Generally, this transesterification route can be described as a two-step process, which involves the first step of the transesterification of DMC with BuOH to form methyl butyl carbonate (MBC) (Eq. (1)) and the second step of the transesterification 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/Al₂O₃ 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*-Bu₂SnO as catalyst. Tang et al. [13] had further investigated the transesterification of DMC with phenol catalyzed by core-shell TiO₂@SiO₂ 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

Tetramethylammonium 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°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°C . The structures of these $[N_{2222}][AA]$ ILs were confirmed by ^1H NMR, elemental analysis and FT-IR spectroscopy, and no impurities were found by ^1H 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°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 biphas, 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°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°C , respectively; the column temperature was increased stepwise to 200°C , holding at 80°C for 2 min, increasing to 200°C at $40^\circ\text{C min}^{-1}$, holding at 200°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.

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

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

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

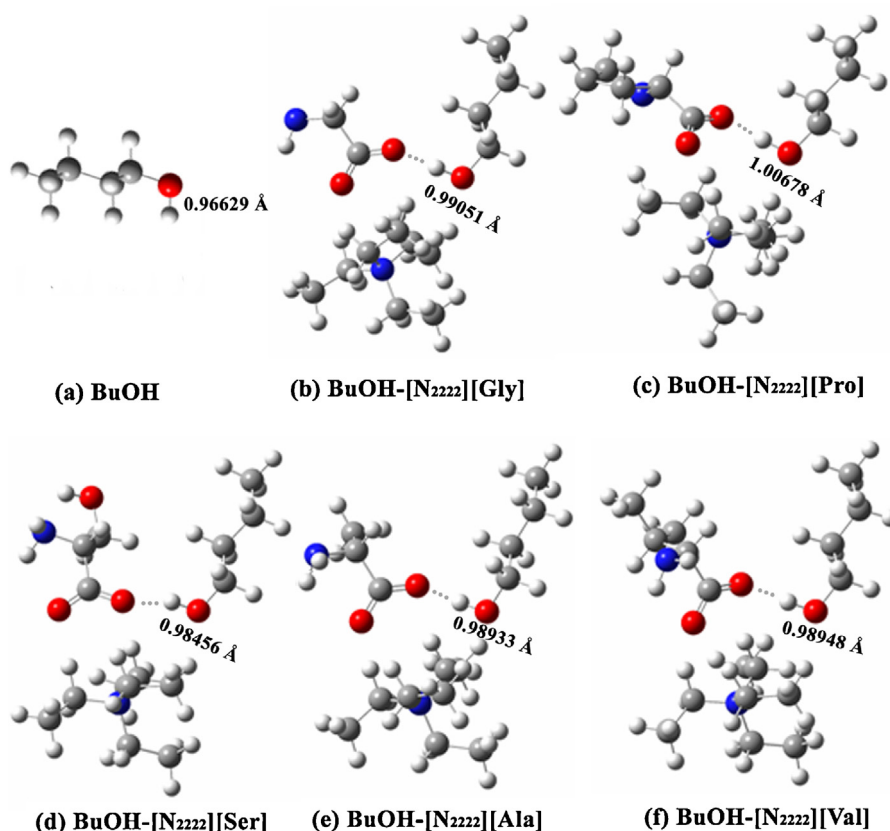


Fig. 1. The O—H bond length of BuOH in the free BuOH and the complexes of BuOH with $[N_{222}][AA]$.

in Table 1. It is obvious that these five $[N_{222}][AA]$ catalysts show different catalytic activities, and the sequence is $[N_{222}][Pro] > [N_{222}][Gly] > [N_{222}][Ala] \approx [N_{222}][Val] > [N_{222}][Ser]$ (entries 1–5). Among $[N_{222}][AA]$ ILs, $[N_{222}][Pro]$ catalyzed the reaction to have the highest conversion of DMC (96%) and selectivity of DBC (75%). In order to illustrate the underlying mechanism, we calculated the geometry optimization for the free BuOH, the complex of BuOH with $[N_{222}][AA]$, and the complex of DMC with $[N_{222}][AA]$ at the B3LYP/6-31++G(d,p) level of theory. Then the binding energies of BuOH- $[N_{222}][AA]$ and DMC- $[N_{222}][AA]$ are given in Table 2, and the corresponding O—H bond lengths of BuOH are shown in Fig. 1. It can be seen that the binding energy of BuOH- $[N_{222}][AA]$ is calculated to be more than -50 kJ/mol,

and all the O—H bond lengths in the BuOH- $[N_{222}][AA]$ complexes are predicted to be stretched and are longer than that in the free BuOH. This indicates that the intermolecular interactions between BuOH and $[N_{222}][AA]$ are strong, and result in an increase in the O—H bond length. Moreover, it is found that $[N_{222}][Pro]$ enables BuOH to have the longest O—H bond length compared with other ILs, owing to its larger binding energies. The binding energy of DMC- $[N_{222}][Pro]$ is also greater than those of other ILs. This demonstrates that $[N_{222}][Pro]$ can activate BuOH and DMC well at the same time, and thus synergistically catalyze the transesterification to have the highest yield of DBC.

Subsequently, we investigated the catalytic activities of other basic carboxylate and proline ILs such as $[N_{222}][Ace]$, $[P_{4444}][Ace]$, $[P_{4444}][Pro]$ and $[N_{1111}][Pro]$ for the synthesis of DBC (entries 6–9). The results showed that all of these ILs performed good DMC conversion but low DBC selectivity compared with $[N_{222}][Pro]$ under the same conditions. Moreover, several typical industrial basic catalysts such as K_2CO_3 , NaOH, triethylamine, and Amberlite-IRA400 resin were employed for comparison. It is also found that these four conventional basic catalysts induced high conversions of DMC but their selectivities of DBC were relatively too low (entries 10–13). This implies that the second step of the

Table 1
Results of transesterification of DMC with BuOH in the presence of different catalysts.^a

Entry	Catalyst	DMC conversion (%)	DBC selectivity (%)
1	$[N_{222}][Pro]$	96	75
2	$[N_{222}][Gly]$	94	31
3	$[N_{222}][Ala]$	92	24
4	$[N_{222}][Val]$	89	22
5	$[N_{222}][Ser]$	37	7
6	$[N_{222}][Ace]$	93	42
7	$[P_{4444}][Pro]$	95	65
8	$[P_{4444}][Ace]$	88	36
9	$[N_{1111}][Pro]$	90	45
10	NaOH	94	30
11	Et_3N	94	37
12	K_2CO_3	95	42
13	Amberlite-IRA400	92	35
14	Proline	46	9

^a Reaction conditions: DMC (20 mmol), BuOH (80 mmol), catalyst (0.5 wt%), reaction temperature ($110^\circ C$), reaction time (4 h).

Table 2
The binding energy of $[N_{222}][AA]$ interaction with DMC and BuOH.

Entry	IL	E (kJ/mol)	
		DMC	BuOH
1	$[N_{222}][Pro]$	−36.87	−77.04
2	$[N_{222}][Gly]$	−31.95	−59.42
3	$[N_{222}][Ala]$	−30.85	−56.03
4	$[N_{222}][Val]$	−27.59	−56.60
5	$[N_{222}][Ser]$	−23.66	−55.05

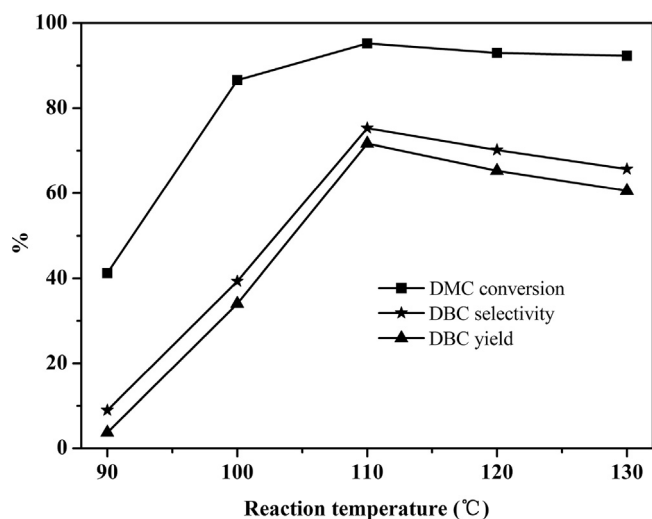


Fig. 2. Effect of reaction temperature on the reaction. Reaction conditions: DMC (20 mmol), BuOH (80 mmol), catalyst (0.5 wt%), reaction time (4 h).

transesterification of MBC with BuOH to form DBC is hard to perform in the presence of these catalysts. In addition, the raw material proline was found to have less catalytic effect to the transesterification reaction, and low DMC conversion and low DBC selectivity were then detected (entry 14). This is because that proline is difficult to soluble in this reactive system and thus hard to contact with the reactants. Thus, it is validated from the comparison of catalytic performance that $[N_{2222}][Pro]$ is considered to be a promising catalyst with high activity and selectivity for the synthesis of DBC. $[N_{2222}][Pro]$ was then chosen as the catalyst for further studies.

3.2. Effects of various reaction conditions on the reaction

In order to obtain the optimum conditions, reaction parameters such as reaction time, temperature, catalyst amount, and initial molar ratio of reactants were studied in detail. Fig. 2 illustrates the catalytic performance of $[N_{2222}][Pro]$ at different temperatures ranging from 90 °C to 130 °C, while reaction was carried out using molar ratio of BuOH to DMC of 4:1 in the presence of 0.5 wt% $[N_{2222}][Pro]$ as catalyst for 4 h. These results suggest that increasing the reaction temperature has a pronounced effect on the activity of the catalyst, as reaction temperature increased from 90 °C to 110 °C, the conversion of DMC and selectivity of DBC also increased. For example, the conversion of DMC increased obviously from 42% to 95% and the selectivity of DBC increased from 4% to 75%, while the temperature increased from 90 °C to 110 °C. However, when the temperature further increased to 120 °C and 130 °C, a sharp decrease in the selectivity of DBC was observed, and the corresponding yields of DBC were reduced to 65% and 60%, respectively. It could be explained that the transesterification reaction of DMC with BuOH is slightly exothermic and the equilibrium constant would decrease with the increase of reaction temperature. High reaction temperature is beneficial to the reverse of transesterification reaction, resulting in a decrease in the yield of DBC. This demonstrates that the overhigh reaction temperature is negative to the yield of DBC, and an optimized temperature for $[N_{2222}][Pro]$ would choose at 110 °C for the efficient synthesis of DBC.

Subsequently, the influence of catalyst amount on the transesterification reaction of DMC with BuOH were investigated at 110 °C, with the reaction time of 4 h and the molar ratio (BuOH/DMC) of 4, and the results are shown in Fig. 3. It is demonstrated that with an increase in the amount of ILs, the total number of base sites available for the reaction increases and thus the rate of transesterification is enhanced, resulting in a higher yield of DBC. For example,

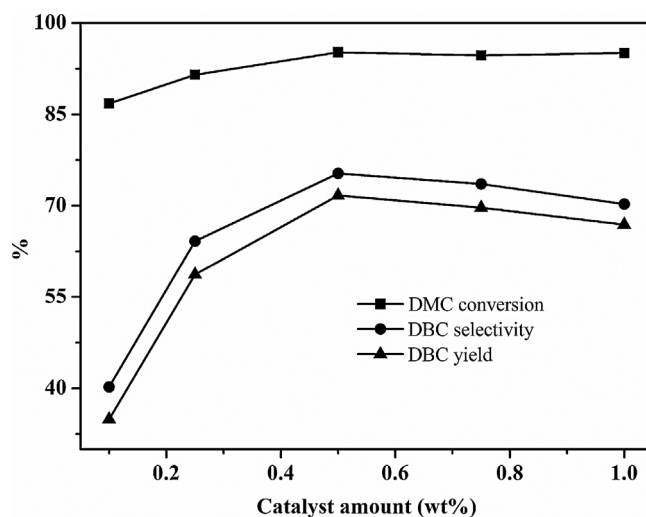


Fig. 3. Effect of catalyst amount on the reaction. Reaction conditions: DMC (20 mmol), BuOH (80 mmol), reaction temperature (110 °C), reaction time (4 h).

the selectivity of DBC increased obviously from 35% to 72% with the increase in the dosage of $[N_{2222}][Pro]$ from 0.1 wt% to 0.5 wt%. However, when the catalyst amount was further added to 0.75 wt% and 1 wt%, respectively, a decrease in the selectivity of DBC was examined while the conversion of DMC did not change significantly. This shows that too much catalyst amount has less impact on the conversion of DMC and is not favorable to the selectivity of DBC. As a consequence, considering the reaction rate and the cost of catalysts, 0.5 wt% is taken as the optimum catalyst loading and used in most of the experiments.

The effect of reaction time on the conversion of DMC and the selectivity of DBC was also evaluated, and the results are given in Fig. 4. The experiments are performed at 110 °C, catalyst amount of 0.5 wt%, and the molar ratio of BuOH/DMC of 4. It is indicated that reaction time has an obvious influence on the reaction, the DMC conversion and DBC selectivity increased in the initial stage and remained almost unchanged between 4 h and 5 h. Nevertheless, the DMC conversion and DBC selectivity began to decrease when the reaction time was further prolonged to 6 h. This may be reasoned that the produced overmuch methanol could promote the reverse reaction with enough time and thus decrease the DMC conversion and DBC selectivity. Thus, it suggests that too long time is not

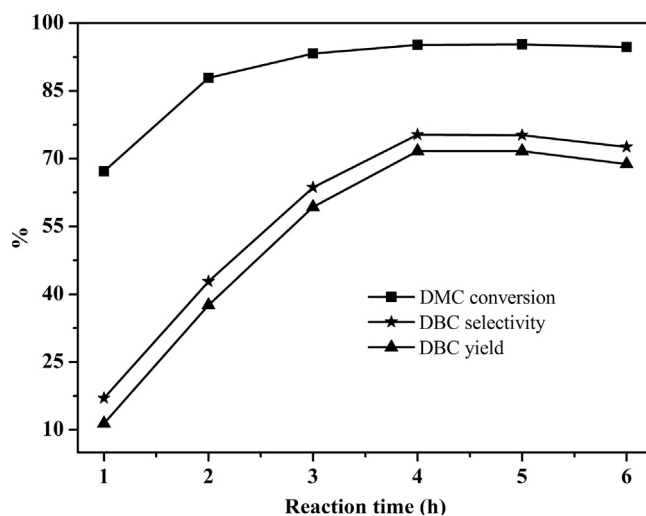


Fig. 4. Effect of reaction time on the reaction. Reaction conditions: DMC (20 mmol), BuOH (80 mmol), catalyst (0.5 wt%), reaction temperature (110 °C).

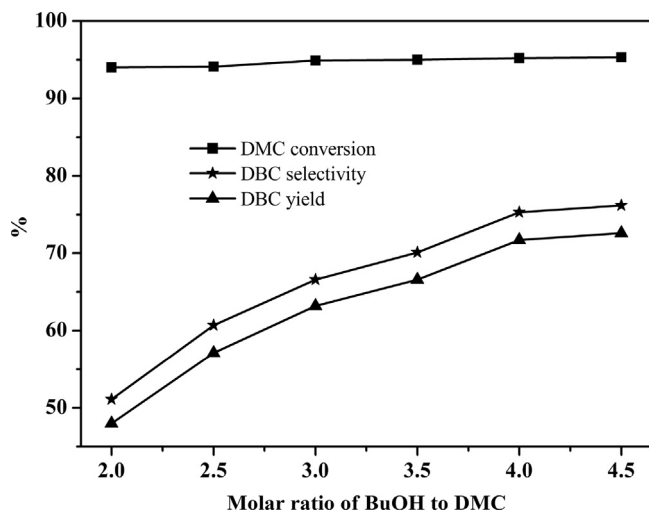


Fig. 5. Effect of molar ratio of BuOH to DMC on the reaction. Reaction conditions: DMC (20 mmol), catalyst (0.5 wt%), reaction temperature (110 °C), reaction time (4 h).

favorable to the forward reaction, and an appropriate reaction time should be chosen at 4 h for the synthesis of DBC. In addition, Fig. 5 represents the effect of molar ratio of BuOH to DMC on the reaction at 110 °C, with the reaction time of 4 h and the catalyst dosage of 0.5 wt%. It is illustrated that as the amount of BuOH increased varying from 2:1 to 4:1, the conversion of DMC and the selectivity of DBC were rapidly improved. However, the molar ratio of BuOH to DMC was greater than 4:1, the yield of DBC did not substantially increase, thereby, the optimal molar ratio of BuOH to DMC is preferred to be 4:1.

3.3. NBO analysis

In order to clarify the synergistic catalysis of $[N_{2222}][Pro]$ in the synthesis of DBC, we further calculated the natural bond orbital (NBO) atomic charges of carbon, hydrogen, and oxygen atoms in the free BuOH and DMC, the complexes of BuOH with $[N_{2222}][Pro]$, and the complexes of DMC with $[N_{2222}][Pro]$ at the B3LYP/6-31++G(d,p) level of theory, respectively (Fig. 6). The electrostatic potential maps of $[N_{2222}][Pro]$ and these complexes are also listed in supplementary data. As can be seen in Fig. 6a, compared with the free BuOH counterpart, the NBO atomic charge of the oxygen atom O (1) in the complexes of BuOH with $[N_{2222}][Pro]$ increased from -0.542 to -0.603 because of the electron-donating effect of the carboxylate group in the $[Pro]$ anion. On the other hand, the hydroxyl group in BuOH shares the negative charge of the oxygen atom in the $[Pro]$ anion and thus the O–H bond lengths is stretched, leading to an increase in the electrophilicity of BuOH. Moreover, Fig. 6b shows NBO atomic charges of C (1), O (2), and O (3) atoms in the free DMC and the complex of DMC with $[N_{2222}][Pro]$. It is obvious that both the NBO positive charge of the carbon atom C (1) and the NBO negative charge of the oxygen atoms O (2) and O (3) increase. This means that the electrophilicity of DMC could improve after the interaction of the free DMC with the secondary amine group of $[N_{2222}][Pro]$, which is in favor of the nucleophilic attack by the activated BuOH. As a result, a high DBC yield can be obtained in the presence of $[N_{2222}][Pro]$. Therefore, $[N_{2222}][Pro]$ is proved to have a dual activation catalysis for BuOH and DMC. The catalytic performance results in Table 1, together with the binding energy in Table 2, provide strong evidence for this hypothesis.

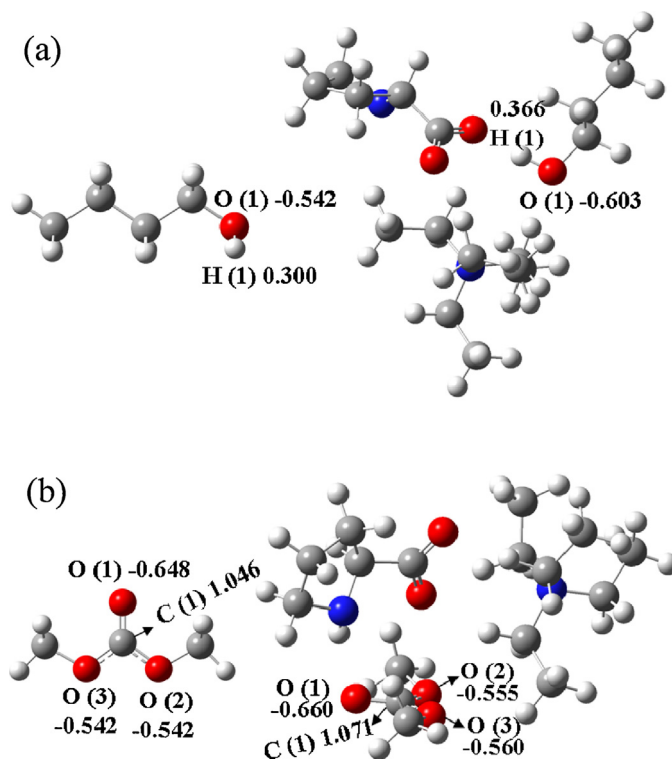


Fig. 6. Optimized structures and NBO charge analysis of (a) free BuOH and the complexes of BuOH with $[N_{2222}][Pro]$ and (b) free DMC and the complexes of DMC with $[N_{2222}][Pro]$.

3.4. Reaction mechanism study

On the basis of the above-mentioned results and the previous literatures [24–26], a plausible mechanistic pathway for the formation of DBC is proposed and then shown in Fig. 7. Firstly, the C=O bond of DMC and the O–H bond of BuOH can be activated by secondary amine group and carboxylate group in $[N_{2222}][Pro]$, respectively, resulting in an active state of DMC and BuOH with the formation of (N–H...O) hydrogen bond and (O–H...O) hydrogen bond. Subsequently, activated BuOH makes nucleophilic attack to the carbonyl-carbon atom of DMC to form MBC and methanol. After that, MBC continues to interact with $[N_{2222}][Pro]$ and reacts with nucleophilic butoxyanion to give DBC. Therefore, it is obviously demonstrated that the synergistic dual activation catalysis of $[N_{2222}][Pro]$ are highly favorable for transesterification reaction and thus catalyze this reaction to have good yields of DBC.

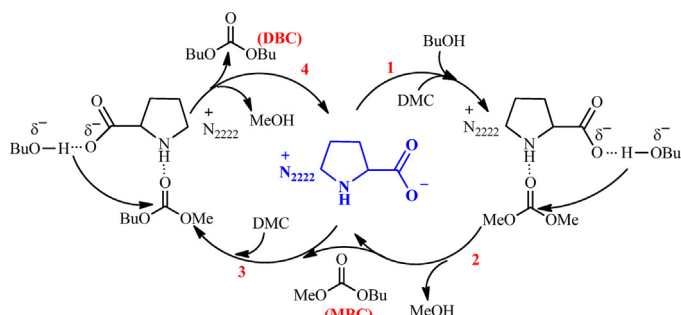


Fig. 7. The plausible reaction mechanism for $[N_{2222}][Pro]$ promoted transesterification.

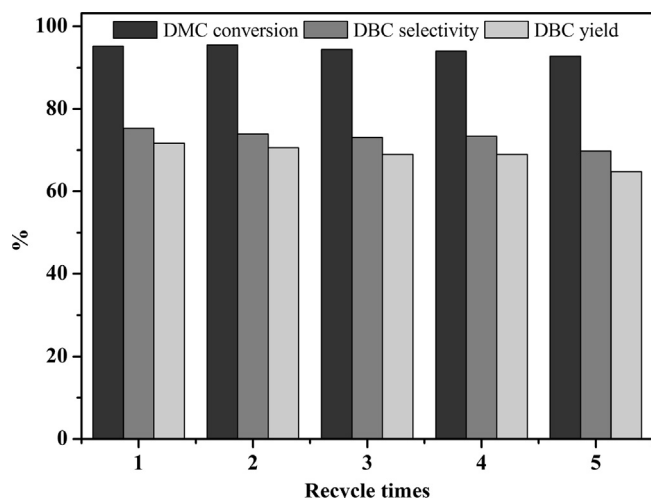


Fig. 8. The recycle test of [N₂₂₂₂][Pro] catalyst.

3.5. Evaluation of catalyst stability

Under the optimum reaction condition, we conducted recycling experiments to examine the recyclability of [N₂₂₂₂][Pro] on the transesterification reaction of DMC with BuOH. As shown in Fig. 8, no significant drop in both the conversion of DMC and the selectivity of DBC is detected after five successive recycles. Also, there is no obvious change in the IR spectra of the fresh catalyst and the recovered catalyst (Fig. S4 in supplementary data). This finding shows that the catalyst [N₂₂₂₂][Pro] for the transesterification is stable enough to be recycled. In addition, the weight recovery results (Table S1 in supplementary data) indicate that after five runs about 7% of [N₂₂₂₂][Pro] catalyst is lost due to the transferring of samples during the regeneration, and this loss is considered to be the main cause for the slight decrease in DMC conversion and DBC selectivity.

3.6. Transesterification reaction of DMC with other alcohols

To obtain more information about other dialkyl carbonates, the transesterification reaction of DMC with other alcohols such as ethanol, propanol, pentanol and phenol in the presence of [N₂₂₂₂][Pro] was also studied, and then the results are listed in Table 3. It is indicated that both DMC conversion and dialkyl carbonate selectivity improve with the increase of carbon chain length of fatty alcohol (entries 1–3). This finding shows that long chain fatty alcohol has the better nucleophilicity to form corresponding dialkyl carbonate, and the reverse reaction of higher dialkyl carbonate is suppressed. In addition, no products were detected in the transesterification of DMC with phenol (entry 4). It should be ascribed to a very small reaction equilibrium constant ($K_p = 3 \times 10^{-4}$ at 453 K), resulting in too low DPC yield [27].

Table 3
Results of transesterification of DMC with other alcohols.^a

Entry	Alcohols	DMC conversion (%)	Dialkyl carbonate selectivity (%)
1	Ethanol	89	44
2	<i>n</i> -Propanol	94	63
3	<i>n</i> -Pentanol	97	81
4	Phenol	–	–

^a Reaction conditions: DMC (20 mmol), alcohol (80 mmol), catalyst (0.5 wt%), reaction temperature (110 °C), reaction time (4 h).

4. Conclusions

In summary, five [N₂₂₂₂][AA] ILs had been synthesized and applied in the synthesis of DBC via the transesterification reaction of DMC with BuOH. Among five ILs, [N₂₂₂₂][Pro] was found to play the best catalytic performance with 96% conversion to DMC and 75% selectivity to DBC, and the optimal condition was set as follows: temperature of 110 °C, reaction time of 4 h, initial molar ratio of 4:1, and catalyst dosage of 0.5 wt%. Quantum-mechanical calculations further manifested that such high DBC yield originated from the synergistic dual activation catalysis of [N₂₂₂₂][Pro]. It was demonstrated that the O–H bond length of BuOH could be stretched and the NBO atomic charge of the carbon atom in DMC was increased by [N₂₂₂₂][Pro], which enhances the electrophilicity of BuOH and the nucleophilicity of DMC respectively, resulting in the excellence yield of DBC. In addition, [N₂₂₂₂][Pro] could be readily recovered and reused up to five times without significant losses in catalytic activity and quantity. Therefore, [N₂₂₂₂][Pro] is considered to be an effective recyclable homogeneous catalyst for the phosgene-free synthesis of DBC and shows potential application in industry.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2014.12.037>.

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