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Dimethyl carbonate synthesis catalyzed by DABCO-derived basic ionic liquids via transesterification of ethylene carbonate with methanol

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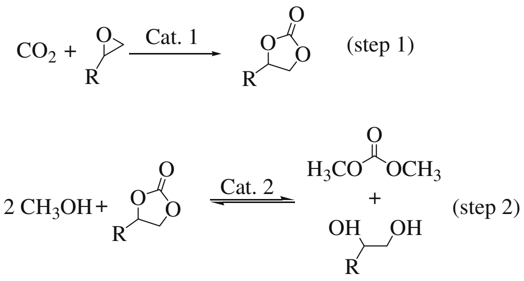
ABSTRACT

Easily prepared DABCO-derived (1,4-diazobicyclo[2.2.2]octane) basic ionic liquids were developed for an efficient synthesis of dimethyl carbonate (DMC) via the transesterification of ethylene carbonate (EC) with methanol. 1-Butyl-4-azo-1-azoniabicyclo[2.2.2]octane hydroxide ([C_4DABCO]OH) exhibited high catalytic activity and 81% DMC yield together with 90% EC conversion was obtained under mild reaction conditions. Notably, the catalyst could be recycled for four times without loss of catalytic activity. Moreover, a possible mechanism was also discussed.

Dimethyl carbonate (DMC) has been drawing much attention as a safe, non-corrosive, and environmentally friendly building block for the production of polycarbonate and other chemicals.[1] Most promisingly, DMC is of interest as an additive to fuel oil owing to a high octane number, reducing particulate emission from diesel engines.[2] In addition, it has been used as an electrolyte in lithium batteries due to its high dielectric constant.[3] Therefore, the development of green and efficient DMC production technology and its fuel properties has attracted much more attention in oil and chemical industries. From the viewpoint of green chemistry, the two-step transesterification process utilizing CO_2 as a raw material, as illustrated in Scheme 1, is more attractive compared with other commercial processes[4] including methanolysis of phosgene, carbon monoxide-nitrite process, and gas-phase oxidative carbonylation of methanol using toxic, corrosive, flammable, and explosive gases.

In the past decades, numerous heterogeneous catalysts have been proposed for the transesterification of alkylene carbonate with methanol, such as molecular sieves,[5] basic metal oxides,[6] metal cyanides,[7] basic salts,[8] dawsonites,[9] hydrotalcites,[10] smectites,[11] basic anion-exchange resin,[12] functionalized chitosan,[13] and silica.[14] In addition, the transesterification reaction also proceeded very efficiently by using homogeneous catalysts including alkali metals,[15] quaternary ammonium salts,[16] and ionic liquids (ILs).[17] Although great advances have been seen,[5–17] most catalytic processes suffer from low catalytic activity, and high CO_2 pressure, high reaction temperature, and/or the use of expensive metallic compounds are often required. So development of more efficient, easily prepared, low cost, and single component catalyst for DMC synthesis is still highly desired.

Because of their distinctive properties such as high thermal stability, negligible vapor pressure, high loading capacity, or ease of recycling, environmental friendliness, ILs have attracted significant attention from the scientific community.[18] Various chemical reactions have been well performed in ionic liquids.[19] However, their use as catalysts for DMC synthesis through transesterification reaction is scarcely available in the literature. Very recently, Ju et al. reported that DMC was successfully prepared from methanol and EC in the presence of 1-alkyl-3-methylimidazolium ionic liquids at 160 °C and 2 MPa CO_2.[17] In the framework of our continuous effort on the synthesis of organic carbonates from CO_2,[13,20,21] herein we would like to report that DMC synthesis via transesterification of EC with methanol was achieved by employing the Lewis basic ILs derived from DABCO as efficient and recyclable catalysts



Scheme 1. Two-step process for DMC production utilizing CO_2 as a raw material.

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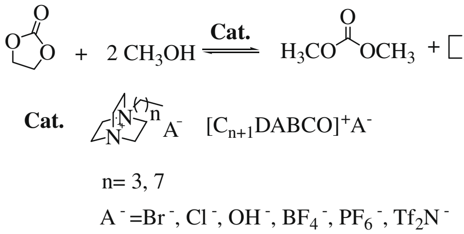


Scheme 2. Lewis basic ionic liquids-catalyzed synthesis of DMC via transesterification of EC with methanol.

(Scheme 2). Interests in DABCO-based ILs would presumably be thanks to facile preparation from commercially available and relatively inexpensive starting materials, gratifyingly thermal behavior, air/water stability. More importantly, methanol could be activated by the tertiary nitrogen of the cation to easily form CH_3O^-.[22] In this context, the Lewis basic ionic liquid $[C_4DABCO]OH$ delightedly displayed high activity for the transesterification of EC with methanol. Excellent EC conversion with high DMC yield was obtained under mild conditions.

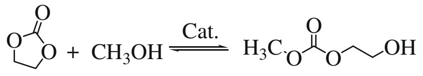
At the initial study, the transesterification of EC with methanol was conducted in the presence of a series of Lewis basic ionic liquids consisting of $C_{n+1}DABCO^+$ ($n = 3, 7$) with various anions (OH^-, Cl^-, Br^-, BF_4^-, PF_6^-, Tf_2N^-). All the experiments were carried out under identical operating conditions and several typical catalysts were also tested (Table 1).

Small amount of DMC could be detected even without any catalyst under the reaction conditions (Table 1, entry 1), whereas most catalysts could greatly improve the reaction (entries 2–14). Gratifyingly, excellent DMC yield and selectivity were achieved by employing a DABCO-based IL, that is, $[C_4DABCO]OH$ as a catalyst after optimizing the reaction conditions (entry 3). Interestingly, both DMC yield and selectivity decreased remarkably as the alkyl length of the cation increasing from C_4 to C_8 (entry 5 vs 6), probably due to reducing hydrophilicity as well as solubility and thus decreasing reactivity of the ionic liquid in methanol as reported by Huddleston and Visser[17,23] The effect of anions on catalyst performance of $C_{n+1}DABCO^+$-based ILs was also investigated. The results revealed that catalytic efficiency increased in the order of $Cl^- < Br^- < OH^-$ ($n = 3$), or $BF_4^- < Br^- < PF_6^- < Tf_2N^-$ in the case of $n = 7$ (entries 2 and 4–9). It is worth mentioning that 2-hydroxyethyl methyl carbonate (HEMC) being regarded as the intermediate for DMC formation (Scheme 3), as detailedly depicted in Scheme 4 (intermediate **II**), was identified by GC and NMR (see the Supplementary data). Specifically, HEMC was indeed found to be the sole product when using $[C_8DABCO]BF_4$ as the catalyst for the transesterification reaction (entry 9).

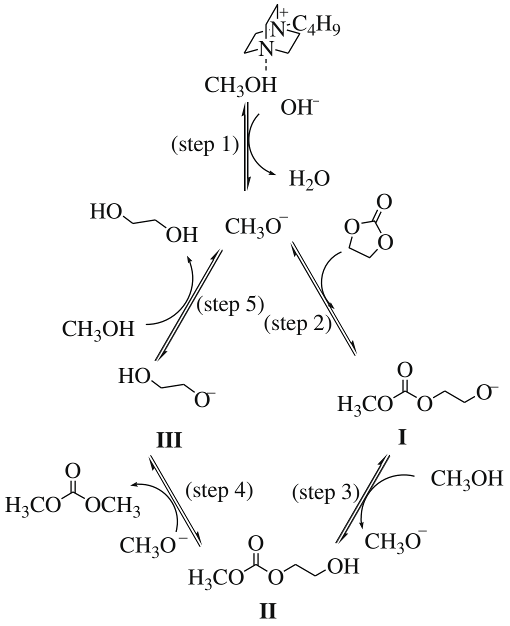
Table 1
DABCO-derived ionic liquids-catalyzed DMC synthesis through transesterification reaction[a]

Entry	Cat.	Conv. (%)	Yield (%)		
			DMC[b]	EG[b]	HEMC[c]
1	No catalyst	15	6	7	7
2	$[C_4DABCO]OH$	72	50	51	14
3[d]	$[C_4DABCO]OH$	90	81	82	5
4	$[C_4DABCO]Cl$	57	25	26	22
5	$[C_4DABCO]Br$	46	26	27	19
6	$[C_8DABCO]Br$	55	22	21	23
7	$[C_8DABCO]PF_6$	58	30	29	22
8	$[C_8DABCO]NTf_2$	55	34	33	21
9	$[C_8DABCO]BF_4$	27	0	0	27
10	[BMIm]Br[e]	56	14	15	24
11	Me_4NBr	76	41	42	13
12	D201-OH[f]	59	36	35	21
13	DABCO	95	84	83	3
14	NaOH	91	73	74	0

[a] Reaction conditions: EC, 10 mmol (0.88 g); methanol, 100 mmol (4 mL); cat., 1 mol % relative to EC; 4 h; 70 °C.
[b] Determined by GC.
[c] HEMC: 2-hydroxyethyl methyl carbonate, monoester product, the intermediate for DMC formation; yields were determined by a combinatorial method of ^1H NMR and GC.
[d] EC, 10 mmol (0.88 g); methanol, 150 mmol (6 mL); cat., 18.7 mg (1 mol %); 6 h; 70 °C.
[e] 1-Butyl-3-methyl imidazolium bromide.
[f] D201-OH: a kind of ion exchange resin, that is, polystyrene with $N^+(CH_3)_3$ HO^- as a functional group (exchange capacity, 3.7 mmol g^{-1}; degree of crosslinking of bead, 1%; bead diameter, 0.3–1.25 mm), supplied from the Chemical Plant of Nankai University.



Scheme 3. The formation of 2-hydroxyethyl methyl carbonate.



Scheme 4. Proposed mechanism for DMC formation.

Furthermore, in comparison with the common basic catalysts, $[C_4DABCO]OH$ showed higher activity than solid D201-OH and the imidazolium-based IL, even higher than the homogeneous ammonium salt (entries 10–12 vs entry 2), which could be decomposed into tributylamine.[24] But strong bases, for example, DABCO and sodium hydroxide as hardly recyclable catalysts showed much higher catalytic activity (entries 13 and 14). In addition, it was also reported that methanol could be activated by Lewis basic species,[21a,25] whereby CH_3O^- formed in situ reacts with EC giving DMC and EG. Therefore, catalytic efficiency could be likely correlated with the basicity of the tested catalysts. Indeed, higher DMC yield was achieved as the basicity of the catalyst increased. Hence, $[C_4DABCO]OH$ was chosen as the model catalyst for further investigation.

Subsequently, the influence of MeOH/EC ratio on the reaction was investigated under the otherwise identical reaction conditions, as shown in Figure 1. Obviously, MeOH/EC ratio has significant impact on the transesterification reaction. As the molar ratio of MeOH/EC varying from 10:1 to 30:1, both DMC yield and EC conversion increased gradually, being presumably attributed to the

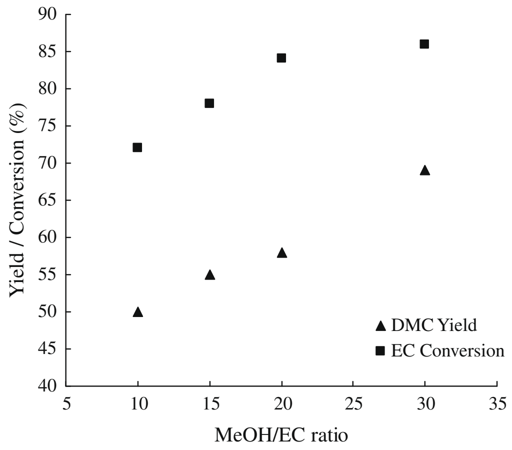


Figure 1. The dependence of DMC yield and EC conversion on MeOH/EC ratio catalyzed by [C_4DABCO]OH. Reaction conditions: EC, 10 mmol (0.88 g); cat., 18.7 mg (1 mol %); 4 h; 70 °C.

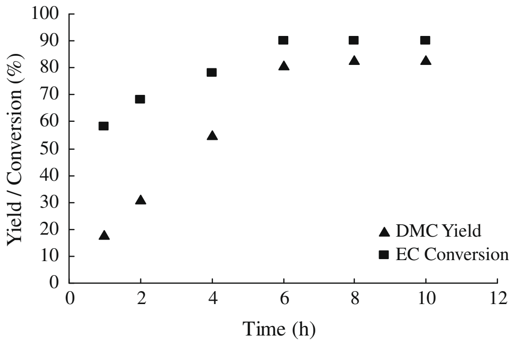


Figure 2. Effect of reaction time on DMC yield and EC conversion using [C_4DABCO]OH as a catalyst. Reaction conditions: EC, 10 mmol (0.88 g); MeOH, 150 mmol (6 mL); cat., 18.7 mg (1 mol %); 70 °C.

reversible nature of the transesterification step.[20] Nevertheless, a suitable value (15:1) was determined in the subsequent investigation in consideration of energy consumption.

The dependence of DMC yield and EC conversion on reaction time was also evaluated. It is found that the reaction time had a strong influence on the reaction. As shown in Figure 2, the reaction rate was faster in the initial stage and remained almost invariant after 6 h. This hints the transesterification reaction reaches equilibrium after ca. 6 h under the reaction conditions. Conclusively, a reaction time of 6 h is appropriate for the synthesis of DMC in this study.

Figure 3 shows the effect of catalyst loading on DMC yield and EC conversion for the catalyst [C_4DABCO]OH. As easily seen, the catalyst amount has a considerable influence on EC conversion in the range of 0.1–1 mol %. It was worth noting that 0.1 mol % catalyst gave low DMC selectivity, probably owing to facile formation of HEMC at low catalyst concentration whereas requirement of higher catalyst loading or strong basic catalysts for further transesterification of intermediate **II** with methoxide to DMC formation. DMC yield (81%) with 90% EC conversion was obtained at 1 mol % of catalyst loading. However, further increasing the catalyst loading to 3 mol % almost did not change DMC yield and EC conversion. As a consequence, a catalyst loading of 1 mol % is enough for this reaction.

It is well known that the stability and reusability of a catalyst system are the two key factors that identify whether it finds potentially practical application in industry. To test catalyst reusability, the reaction was carried out under the optimum conditions in the presence of catalytic amount of [C_4DABCO]OH. The catalyst was recovered after separation of DMC/ethylene glycol from the reaction mixture by distillation and then used for the next run under the same conditions. The results as listed in Table 2 indicated that no significant drop in either DMC yield or selectivity was detected after four successive recycles.

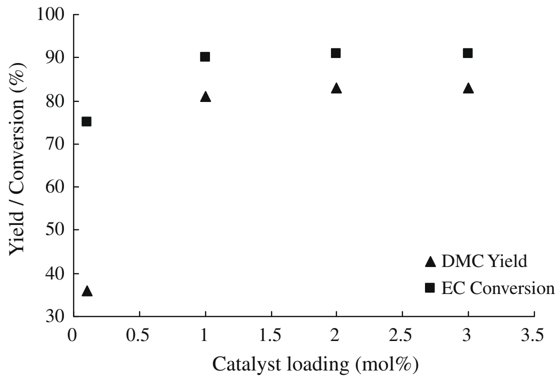


Figure 3. Influence of catalyst loading on DMC yield and EC conversion using [C_4DABCO]OH as a catalyst. Reaction conditions: EC, 10 mmol (0.88 g); MeOH, 150 mmol (6 mL); 6 h; 70 °C.

Table 2
The catalyst reusability[a]

Cycle	Conv. (%)	Yield of DMC (%)
1	90	81
2	89	80
3	92	79
4	88	79

[a] Reaction conditions: EC, 10 mmol (0.88 g); MeOH, 150 mmol (6 mL); cat., [C_4DABCO]OH, 18.7 mg (1 mol %), 6 h; 70 °C.

Table 3
The process for dialkyl carbonate synthesis using different alcohols[a]

Entry	Alcohol	Conv. (%)	Yield of DAC[b] (%)
1	MeOH	90	81
2	EtOH	66	42
3	^{i}PrOH	57	4
4	^{t}BuOH	21	17

[a] Reaction conditions: ethylene carbonate, 10 mmol (0.88 g); alcohol, 150 mmol; cat., [C_4DABCO]OH, 18.7 mg (1 mol %), 6 h; 70 °C.
[b] DAC: dialkyl carbonate.

Various alcohols, that is, methanol, ethanol, *iso*-propanol, and *tert*-butanol were also tested through the present process for the synthesis of dialkyl carbonates (DAC). As shown in Table 3, the tested alcohols were transesterified with EC to the corresponding DAC, except that only quite low DAC yield was obtained in the case of ^{i}PrOH, presumably due to its steric hindrance. However, the selectivity of DAC was better for the bulky substrate, for example, ^{t}BuOH in comparison with ^{i}PrOH, although the reactivity was low (entry 4).

Based on the published reports,[21,25,26] and the results in this study, a probable catalytic cycle was proposed as depicted in Scheme 4. First, the MeOH activated by cage-like tertiary nitrogen of DABCO-derived basic ILs reacts with OH^- to form CH_3O^- (step 1); then, the formed anion attacks carbonyl carbon of EC and thus intermediate **I** is generated (step 2); subsequently, intermediate **II** (HEMC), that is, monoester product, is formed while proton of

MeOH is captured by intermediate **I** (step 3); further nucleophilic substitution of intermediate **II** by CH_3O^- produces DMC and ethylene glycol anion (intermediate **III**) (step 4); ultimately, EG is generated by proton exchange between intermediate **III** and MeOH (step 5). The whole process is assumed to be reversible. This proposed mechanism could account for catalytic efficiency dependence on the structure of the ILs (Table 1, entries 2–9), viz cation and anion effect. Particularly, step 4 is proposed to be more difficult than step 2. Therefore it is reasonable that less basic catalyst could give more monoester product, that is, intermediate **II**, and low catalyst concentration leads to facile formation of HEMC. Please also note that generated EG can be reused for EC synthesis.[17]

In conclusion, a kind of DABCO-based basic ionic liquids, for example, $[C_4DABCO]OH$ was found to be a highly efficient and recyclable catalyst for DMC synthesis through the transesterification reaction of EC with methanol under mild reaction conditions. The ionic liquids used in this study represent as air stable, easily synthesized, cheap, extremely robust, and environmentally benign catalysts, which can effectively activate methanol through tertiary nitrogen in the cation part of the IL in combination with hydroxide anion. The catalyst could be recycled for four times without loss of yield and selectivity. Therefore, this green process could show much potential application in industry. Further extending application of Lewis basic ionic liquids toward other reactions is currently under investigation in our laboratory.

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Supplementary data

Supplementary data (experimental details and characterization data and charts for the prepared catalysts and the intermediate) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.03.114.

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