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# Synthesis of dimethyl carbonate from methanol and CO<sub>2</sub> under low pressure†

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A mild and highly efficient approach has been developed for the direct synthesis of dimethyl carbonate (DMC) from methanol and CO<sub>2</sub> under low initial pressure. The key to a successful transformation is the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), CH<sub>2</sub>Br<sub>2</sub> and ionic liquid. Under the optimized reaction conditions, the yield of DMC was obtained up to 81% under 0.25 MPa. The direct synthesis of DMC can be carried out at balloon pressure using CH<sub>2</sub>Br<sub>2</sub> and DBU. In this case, after the reaction, DBU was proved to be recyclable after having been treated with KOH in ethanol. In addition, a plausible mechanism for this synthetic reaction was proposed according to the experimental results.

## 1. Introduction

With the continuous development of the greenhouse effect, the excessive emission of CO<sub>2</sub>, one of the main causes of this effect, has attracted widespread attention.<sup>1</sup> The effective use of CO<sub>2</sub> for the benefit of mankind has always been one of the focuses of scientists since CO<sub>2</sub> is a non-toxic, abundant, and economical C1 chemical source. Among these uses, the capture of CO<sub>2</sub>,<sup>2</sup> activation and conversion of CO<sub>2</sub> (ref. 3 and 4) are the most attractive. Converting CO<sub>2</sub> to dimethyl carbonate (DMC) is an important direction for the effective use of CO<sub>2</sub> since this conversion has a 100% atom economy and conforms to the concept of Green Chemistry.<sup>5,6</sup> DMC is a green chemical product with a wide range of uses since it is an eco-friendly solvent and versatile intermediate. It can replace toxic dimethyl sulfate, methyl iodide, and phosgene as methylation reagents and carbonylation reagents.<sup>7</sup> It is deemed to be a gasoline additive in place of methyl *tert*-butyl ether (MTBE) to increase the gasoline octane number.<sup>8</sup> Besides, DMC can also be used as an additive for electrolytes in lithium batteries and as a solvent for dopes and inks.<sup>9</sup> In 1992, it was listed as a non-toxic product in Europe. Therefore, the development of efficient and green synthetic routes for DMC has attracted extensive attention.

So far, various methods have been reported to synthesize DMC, including methanol phosgenation, oxidative carbonylation of methanol, urea alcoholysis, two-step transesterification, one-pot synthesis, and direct synthesis. Methanol phosgenation was the unique commercialized available method for producing DMC until 1980. Nonetheless, it is limited due to the employment of toxic and hazardous phosgene.<sup>10</sup> The synthesis of DMC

by oxidative carbonylation of methanol has improved the yield and atom utilization.<sup>11</sup> However, it is recognized that the reaction mixture is highly flammable and hazardous. In recent years, the preparation of DMC by urea alcoholysis has been developed.<sup>12</sup> In this process, thermodynamic limitations and ammonia interferences should be concerned although this method is environmentally friendly. In the first step of transesterification method cyclic carbonate was produced using CO<sub>2</sub> and epoxide as starting materials,<sup>13,14</sup> and then reacted with methanol to produce DMC and the corresponding 1,2-diols.<sup>15</sup> High energy consumption and investment occurred by the separation of intermediate products in two-step transesterification. One-pot synthesis of DMC has been proposed as an alternative route,<sup>16,17</sup> but this method is generally accompanied by side reactions. Given the disadvantages mentioned above, the direct synthesis of DMC from methanol and CO<sub>2</sub> is more attractive in terms of green technology, atomic utilization, and cost.

On account of the high stability of CO<sub>2</sub> and the limitation of thermodynamic equilibrium, direct synthesis of DMC is subjected to two problems: extreme operating conditions and low conversion. Therefore, the capture and activation of CO<sub>2</sub> are the key issues to achieve this transformation, and catalysts and activators play an extremely important role in the process. To date, numerous catalysts and activators for this transformation have been reported, including metal carbonates,<sup>18</sup> organotin compounds,<sup>19</sup> metal oxides,<sup>20,21</sup> dehydrating agent<sup>22–29</sup> and ionic liquids (ILs),<sup>30–32</sup> *etc.* A list of the literature reported systems for the synthesis of DMC has been provided in the ESI (Table S1†). Although many efforts have been made for direct synthesis of DMC, these methods usually encounter with high reaction temperature, long reaction time, high pressure, and low production efficiency. ILs can be used as CO<sub>2</sub> adsorbents due to their special physical and chemical properties. By selecting appropriate cations and anions, the solubility of CO<sub>2</sub> in the reaction solution can be improved.<sup>33</sup> A bi-component system of

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tri-cationic **ILs**/super base was developed by Chaugule *et al.*<sup>34</sup> and a 37.1% conversion of CH<sub>3</sub>OH was obtained at 130 °C under 7.5 MPa CO<sub>2</sub>. It is reported that DBU can capture and activate CO<sub>2</sub> and produce an amidinium alkyl carbonate intermediate [DBUH]<sup>+</sup>[OCOOR]<sup>-</sup> in the presence of alcohol.<sup>35–38</sup> Lim *et al.*<sup>39</sup> reported that CH<sub>2</sub>Br<sub>2</sub> was a unique solvent in the synthesis of dibenzyl carbonate from benzyl alcohol and CO<sub>2</sub>. Later, Zhao *et al.*<sup>40</sup> found that CH<sub>2</sub>Br<sub>2</sub> was the optimum solvent for the direct synthesis of DMC in the presence of imidazolium bicarbonate [(CnCmIm)<sup>+</sup>[HCO<sub>3</sub>]<sup>-</sup>]. Therefore, the combination of DBU and CH<sub>2</sub>Br<sub>2</sub> is expected to play a crucial role in the efficient transformation of DMC from CO<sub>2</sub> and methanol in the presence of **ILs**. In this paper, we report a mild and efficient approach for direct synthesis of DMC from methanol and CO<sub>2</sub> under low initial pressure in the presence of CH<sub>2</sub>Br<sub>2</sub>, DBU, and ionic liquid. The reaction can be carried out under balloon pressure, providing a green process with more application prospects for direct synthesis of DMC.

## 2. Experimental section

### 2.1 Materials

CO<sub>2</sub> was purchased from Dalian Guangming Special Gas Co., Ltd. The other commercially available starting materials were purchased and used without any prior purification unless otherwise indicated.

### 2.2 Techniques used

NMR spectra were recorded on a Bruker Advance II 400 spectrometer using TMS as an internal standard (400 MHz for <sup>1</sup>H NMR). ESI-MS were obtained on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Gas chromatography (GC) analysis was recorded on a gas chromatograph (Agilent 7820) equipped with a capillary column (HP-5, 30 m × 320 μm × 0.25 μm) using a flame ionization detector with a flow rate of 1 mL min<sup>-1</sup> using the following method: the oven temperature was held at 50 °C for 5 min and then increased linearly to 240 °C over 20 min with a final hold of 5 min.

### 2.3 General procedure for the direct synthesis of DMC

For the direct synthesis of DMC, the reactions were conducted in a 25 mL stainless-steel autoclave equipped with a magnetic stirrer and automatic temperature control system. A typical reaction was carried out as follows: an appropriate amount of CO<sub>2</sub> was charged to an autoclave containing a mixture of CH<sub>3</sub>OH (1.0 mmol), 1-ethyl-3-methylimidazole hexafluoro-phosphate (**IL**, 1.0 mmol), DBU (1.5 mmol), CH<sub>2</sub>Br<sub>2</sub> (3.0 mmol) and CH<sub>3</sub>CN (0.3 mL) at room temperature. Then, the autoclave was placed in an oil bath pre-heated to the designated temperature. After stirred for a period the autoclave was cooled down to room temperature, and the remaining CO<sub>2</sub> was removed slowly. The reaction mixture was analyzed by GC using biphenyl as an internal standard.

## 3. Results and discussion

### 3.1 Effect of solvent on the direct synthesis of DMC

Direct synthesis of DMC from CH<sub>3</sub>OH and CO<sub>2</sub> in the presence of DBU and **IL** was carried out systematically. The solvents were

first screened under the conditions of oil bath temperature 60 °C, initial pressure 0.25 MPa, reaction time 6 h, methanol 1.0 mmol, DBU 1.0 equivalent and **IL** 1.0 equivalent. The experimental results are shown in Table 1. The conversion of methanol was 50% and the yield of DMC was 42% in CH<sub>2</sub>Br<sub>2</sub> (Table 1, entry 1). The DMC yield was only 16% in CH<sub>2</sub>Cl<sub>2</sub> (Table 1, entry 2). The conversions of methanol were above 71% in CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>Br and CH<sub>3</sub>CH<sub>2</sub>Br, and the yields of DMC were 6% and 4%, respectively (Table 1, entries 3 and 4). Butyl methyl carbonate (BMC) and dibutyl carbonate were found as byproducts in CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>Br, and the byproducts in CH<sub>3</sub>CH<sub>2</sub>Br were ethyl methyl carbonate (EMC) and diethyl carbonate, analyzed by GC-MS. It was found that no DMC was generated in CH<sub>3</sub>CN, THF and DMF (Table 1, entries 5–7). In summary, CH<sub>2</sub>Br<sub>2</sub> was selected as the solvent to carry out the reaction.

### 3.2 Effect of CH<sub>2</sub>Br<sub>2</sub> volume and DBU loadings on the direct synthesis of DMC

The effect of CH<sub>2</sub>Br<sub>2</sub> volume and DBU loading on the direct synthesis of DMC has been investigated and the results are shown in Table 2. It can be seen from the results that the conversion of methanol was 58% and the yield of DMC was 50% using 0.5 mL CH<sub>2</sub>Br<sub>2</sub> (Table 2, entry 1). Increasing the volume of CH<sub>2</sub>Br<sub>2</sub> to 1.0 mL, the methanol conversion and the DMC yield were 57% and 48%, respectively (Table 2, entry 2). The conversion and the yield did not increase on further increasing the volume of CH<sub>2</sub>Br<sub>2</sub> (Table 2, entries 3–5). No DMC was generated in the absence of DBU (Table 2, entry 6). The yield of DMC increased from 25 to 62% in the range of DBU loadings from 0.50 to 1.50 molar equiv (Table 2, entries 1, 7–9). Further increasing the DBU loading to 1.75 molar equiv did not lead to an increase in DMC yield (Table 2, entry 10). In summary, 0.5 mL of CH<sub>2</sub>Br<sub>2</sub> and 1.50 molar equiv of DBU were considered to be the optimal reaction conditions on the direct synthesis of DMC.

Table 1 Effect of solvent on the direct synthesis of DMC<sup>a</sup>

Entry	Solvent	Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	CH <sub>2</sub> Br <sub>2</sub>	50	42
2	CH <sub>2</sub> Cl <sub>2</sub>	27	16
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	78	6
4	CH <sub>3</sub> CH <sub>2</sub> Br	71	4
5	CH <sub>3</sub> CN	2	0
6	THF	1	0
7	DMF	0	0

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, **IL** 1.0 mmol, DBU 1.0 mmol, solvent 2.0 mL, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C, 6 h. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique.

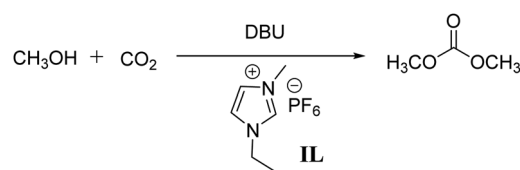


Table 2 Effect of CH<sub>2</sub>Br<sub>2</sub> volume and DBU loadings on the direct synthesis of DMC<sup>a</sup>

Entry	CH <sub>2</sub> Br <sub>2</sub> (mL)	DBU (equiv)	Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Sel. (%)
1	0.5	1.00	58	50	86
2	1.0	1.00	57	48	84
3	1.5	1.00	53	44	84
4	2.0	1.00	50	42	84
5	2.5	1.00	51	42	83
6	0.5	0	3	0	0
7	0.5	0.50	32	25	61
8	0.5	1.25	64	55	86
9	0.5	1.50	72	62	86
10	0.5	1.75	72	62	86

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, **IL** 1.0 mmol, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C, 6 h. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique.

### 3.3 Effect of initial pressure and oil bath temperature on the direct synthesis of DMC

The influence of initial pressure and oil bath temperature on the direct synthesis of DMC has been investigated and the results are shown in Table 3. It can be seen from the results that when the initial pressure was 0.15 MPa, the conversion of methanol was 61% and the yield of DMC was 43% (Table 3, entry 1). At 0.25 MPa, the methanol conversion and the DMC yield were increased to 72% and 62%, respectively (Table 3, entry 2). After that, the yield of DMC showed a downward trend as the initial pressure increased from 0.25 to 1.50 MPa (Table 3, entries 2–5). It is speculated that the reason for this phenomenon may be related to the dilution effect. As the initial pressure increases, excess CO<sub>2</sub> in the reaction system will reduce the concentration of methanol near the DBU.<sup>41,42</sup> When the oil bath temperature was 25 °C, the methanol conversion and the DMC yield were only 17% and 8%, respectively (Table 3, entry 6). This result indicates that a lower temperature is not conducive to the reaction. When the temperature was lower than 60 °C, the DMC yield gradually increased with the increase of temperature

Table 3 Effect of initial pressure and oil bath temperature on the reaction<sup>a</sup>

Entry	Initial pressure		Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Sel. (%)
	(MPa)	T (°C)			
1	0.15	60	61	43	71
2	0.25	60	72	62	86
3	0.50	60	69	57	83
4	1.00	60	66	53	80
5	1.50	60	65	52	80
6	0.25	25	17	8	47
7	0.25	40	37	22	59
8	0.25	50	65	52	80
9	0.25	70	70	60	86
10	0.25	80	64	56	87
11	0.25	100	61	52	85

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, **IL** 1.0 mmol, DBU 1.5 mmol, CH<sub>2</sub>Br<sub>2</sub> 0.5 mL, 6 h. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique.

(Table 3, entries 6–8). At 60 °C, the yield of DMC reached a maximum of 62% (Table 3, entry 2). When the temperature was higher than 60 °C, the yield of DMC decreased (Table 3, entries 9–11). The reason may be that as the temperature increases, the solubility of CO<sub>2</sub> in the solution will decrease, thereby reducing the efficiency of DBU in combination with CO<sub>2</sub>. In addition, high temperatures will promote some side reactions, such as the decomposition of DMC into some gaseous products.<sup>43</sup> Hence, it is considered that 0.25 MPa and an oil bath temperature of 60 °C were selected as the optimal conditions for direct synthesis of DMC.

### 3.4 Effect of IL loading on the direct synthesis of DMC

The effect of **IL** loading on the direct synthesis of DMC has been investigated and the results are shown in Table 4. It can be seen that the yield of DMC was 21% in the absence of **IL** (Table 4, entry 1). The DMC yield increased from 34 to 62% in the range of **IL** loading increasing from 0.25 to 1.00 molar equiv (Table 4, entries 2–5). After that, on further increasing the **IL** loading, the DMC yield did not increase anymore (Table 4, entries 6 and 7). Therefore, an **IL** loading of 1.00 equiv was considered to be the optimal reaction condition.

### 3.5 Effect of the reaction time on the direct synthesis of DMC

Reaction times in the range of 3–18 h have been tested and the results are shown in Fig. 1. It can be seen that the methanol conversion and the DMC yield would gradually increase with the extension of the reaction time. When the reaction time was 12 h, an 81% conversion of methanol and a 73% yield of DMC were obtained. On further prolonging the reaction time to 18 h, the yield of DMC remained roughly constant. Therefore, a reaction time of 12 h was considered to be the optimal reaction time for direct synthesis of DMC.

### 3.6 Effect of the loading of CH<sub>2</sub>Br<sub>2</sub> as an additive on the direct synthesis of DMC

In the case of CH<sub>2</sub>Br<sub>2</sub> as the solvent, the effect of CH<sub>2</sub>Br<sub>2</sub> volume on the reaction was investigated (see Table 2). It was found that the smaller the volume, the higher the DMC yield. However, further decreasing the volume of solvent less than 0.5 mL, the reaction mixture was sticky and not conducive to the progress of

Table 4 Effect of **IL** loading on the direct synthesis of DMC<sup>a</sup>

Entry	<b>IL</b> (equiv.)	Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Sel. (%)
1	0	40	21	52
2	0.25	48	34	71
3	0.50	59	43	73
4	0.75	66	55	83
5	1.00	72	62	86
6	1.25	72	62	86
7	1.50	73	63	86

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, DBU 1.5 mmol, CH<sub>2</sub>Br<sub>2</sub> 0.5 mL, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C, 6 h. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique.



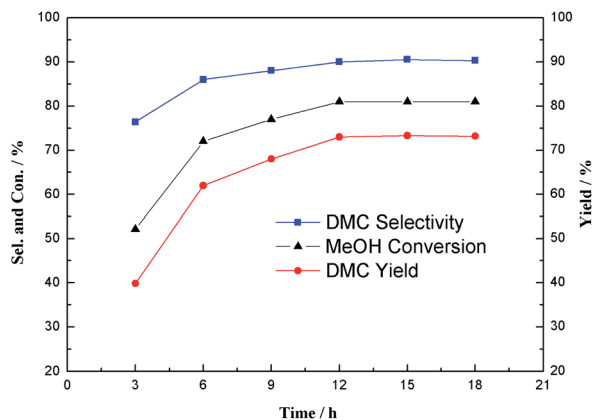


Fig. 1 Effect of the reaction time on the direct synthesis of DMC. Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, IL 1.0 mmol, DBU 1.5 mmol, CH<sub>2</sub>Br<sub>2</sub> 0.5 mL, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C. The yield of DMC was determined by GC using an internal standard technique.

this reaction. Thus, the volume of solvent was screened to a minimum of 0.5 mL (Table 2, entry 1). In this section, the effect of the loading of CH<sub>2</sub>Br<sub>2</sub> as an additive on this reaction was investigated in detail. The results are shown in Table 5. It can be seen from the results that no DMC was formed without CH<sub>2</sub>Br<sub>2</sub> when 0.5 mL CH<sub>3</sub>CN was used as a solvent (Table 5, entry 2). The DMC yield increased from 54% to 77% as the loading of CH<sub>2</sub>Br<sub>2</sub> increased from 1.0 to 3.0 mmol (Table 5, entries 3–5). Further increasing the CH<sub>2</sub>Br<sub>2</sub> loading to 6.0 mmol did not lead to an increase in DMC yield (Table 5, entries 6–8). The yield of DMC was slightly reduced in DMF or Toluene (Table 5, entries 9 and 10). The conversion of CH<sub>3</sub>OH was 76% and the yield of DMC was 65% using 0.1 mL CH<sub>3</sub>CN in the presence of 3.0 mmol CH<sub>2</sub>Br<sub>2</sub> (Table 5, entry 11). Increasing the volume of CH<sub>3</sub>CN to 0.3 mL, the CH<sub>3</sub>OH conversion and the DMC yield were 83% and 81%, respectively (Table 5, entry 12). Further increasing the volume of CH<sub>3</sub>CN the conversion and the yield did not increase (Table 5, entries 13 and 14). Thus, 0.3 mL

Table 5 Effect of the loading of CH<sub>2</sub>Br<sub>2</sub> as an additive<sup>a</sup>

Entry	Solvent (mL)	CH <sub>2</sub> Br <sub>2</sub> (mmol)	Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Sel. (%)
1	—	7.1 (0.5 mL)	81	73	90
2	CH <sub>3</sub> CN (0.5)	0	4	0	0
3	CH <sub>3</sub> CN (0.5)	1.0	56	54	96
4	CH <sub>3</sub> CN (0.5)	2.0	62	60	97
5	CH <sub>3</sub> CN (0.5)	3.0	79	77	97
6	CH <sub>3</sub> CN (0.5)	4.0	78	77	98
7	CH <sub>3</sub> CN (0.5)	5.0	78	77	98
8	CH <sub>3</sub> CN (0.5)	6.0	79	76	96
9	DMF (0.5)	3.0	78	76	97
10	Toluene (0.5)	3.0	76	73	96
11	CH <sub>3</sub> CN (0.1)	3.0	76	65	86
12	CH <sub>3</sub> CN (0.3)	3.0	83	81	98
13	CH <sub>3</sub> CN (0.7)	3.0	74	73	98
14	CH <sub>3</sub> CN (0.9)	3.0	53	51	96

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, IL 1.0 mmol, DBU 1.5 mmol, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C, 12 h. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique.

of CH<sub>3</sub>CN and 3.0 mmol of CH<sub>2</sub>Br<sub>2</sub> were selected as the optimal conditions for the synthesis of DMC.

### 3.7 Effect of the molecular structures of various ILs on the direct synthesis of DMC

Under the optimal conditions of oil bath temperature 60 °C, initial pressure 0.25 MPa, reaction time 12 h, methanol

Table 6 Effect of the molecular structures of ILs on the direct synthesis of DMC<sup>a</sup>

Entry	ILs	Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Sel. (%)
1		83	81	98
2		73	67	92
3		78	70	90
4		82	79	96
5		80	69	86
6		82	70	85
7		72	60	83
8		54	50	93
9		59	44	75
10		65	35	54
11		83	80	96

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, ILs 1.0 mmol, DBU 1.5 mmol, CH<sub>3</sub>CN 0.3 mL, CH<sub>2</sub>Br<sub>2</sub> 3.0 mmol, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C, 12 h. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique.



1.0 mmol, DBU 1.5 mmol, **ILs** 1.0 mmol, CH<sub>3</sub>CN 0.3 mL, and CH<sub>2</sub>Br<sub>2</sub> 3.0 mmol, the effects of the molecular structures of various **ILs** on the direct synthesis of DMC have been investigated and the results are shown in Table 6. The influence of different anions on the reaction was investigated in the case of the same cation, and the **IL** with hexafluorophosphate was the most effective (Table 6, entries 1–8). The effect of the length of the alkyl chain on the cation was investigated in the case of the same anion, and the longer the carbon chain, the lower the yield of the product (Table 6, entries 7 and 9). The presence of hydroxyl group on the cation increased the methanol conversion but was not conducive to the formation of the product (Table 6, entries 8 and 10). When the anion was hexafluorophosphate, the presence of alkyl or benzyl group in the cation had little effect on the reaction (Table 6, entries 1 and 11).

### 3.8 Direct synthesis of DMC under balloon pressure

The previous results show that the CH<sub>3</sub>OH conversion and the DMC yield were 61% and 43%, respectively at 0.15 MPa (Table 3, entry 1). Thus, the direct synthesis of DMC under balloon pressure has been studied and the results are shown in Table 7. Reaction times in the range of 10–15 h have been tested in the presence of **IL**. The yield of DMC reached a maximum of 62% in 12 h (Table 7, entry 2). On further prolonging the reaction time to 15 h, the yield of DMC kept constant (Table 7, entry 3). The DBU loading was investigated in 2 h without **IL**. The yield of DMC increased from 18 to 23% in the range of DBU loadings from 1.00 to 1.25 molar equiv (Table 7, entries 4 and 5). Further increasing the DBU loading to 1.50 molar equiv did not lead to an increase in DMC yield (Table 7, entry 6). Reaction times in the range of 1–6 h have been tested in the presence of 1.25 mmol DBU. The DMC yields in 2 h and 1 h were 23% and 16%, respectively (Table 7, entries 5 and 7). On further prolonging the reaction time to 6 h, the yield of DMC increased slightly (Table 7, entries 8 and 9). Considering the issue of energy consumption, a reaction time of 2 h was considered to be the optimal condition for direct synthesis of DMC under balloon pressure without **IL**.

### 3.9 The reusability of DBU under balloon pressure

The reusability of DBU under balloon pressure has been investigated, and the results are shown in Table 8. When the

Table 7 Direct synthesis of DMC under balloon pressure<sup>a</sup>

Entry	DBU (mmol)	Time (h)	Con. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Sel. (%)
1 <sup>d</sup>	1.50	10	60	58	97
2 <sup>d</sup>	1.50	12	64	62	97
3 <sup>d</sup>	1.50	15	64	62	97
4	1.00	2	32	18	56
5	1.25	2	33	23	70
6	1.50	2	33	23	70
7	1.25	1	27	16	59
8	1.25	4	35	24	69
9	1.25	6	37	24	65

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, CH<sub>3</sub>CN 0.3 mL, CH<sub>2</sub>Br<sub>2</sub> 3.0 mmol, CO<sub>2</sub> balloon, 60 °C. <sup>b</sup> Conversion of CH<sub>3</sub>OH. <sup>c</sup> Yield of DMC determined by GC using an internal standard technique. <sup>d</sup> **IL** 1.0 mmol.

Table 8 The reusability of DBU under balloon pressure<sup>a</sup>

Entry	Base	Loading (mmol)	DMC <sup>b</sup> (%)
1	KOH	0.50	6
2	KOH	0.75	10
3	KOH	1.00	13
4	KOH	1.25	21
5	KOH	1.50	16
6 <sup>c</sup>	KOH	1.25	20
7 <sup>d</sup>	KOH	1.25	18

<sup>a</sup> Reaction conditions: CH<sub>3</sub>OH 1.0 mmol, DBU 1.25 mmol, CH<sub>3</sub>CN 0.3 mL, CH<sub>2</sub>Br<sub>2</sub> 3.0 mmol, CO<sub>2</sub> balloon, 60 °C, 2 h. <sup>b</sup> Yield of DMC determined by GC using an internal standard technique. <sup>c</sup> 2nd run. <sup>d</sup> 3rd run.

reaction was finished, the acetonitrile, methanol, CH<sub>2</sub>Br<sub>2</sub>, DMC and other components in the reaction solution were removed by distillation under reduced pressure. After that, KOH in 3.0 mL ethanol was added to the residue, and the mixture was filtered after stirred at 70 °C for 3 h. Ethanol in the filtrate was removed by vacuum distillation, and the residue containing DBU was directly used in the next run. The DMC yield increased from 6 to 21% in the range of KOH loadings increasing from 0.50 to 1.25 mmol (Table 8, entries 1–4). The DMC yield was 16% in the presence of 1.50 mmol KOH (Table 8, entry 5). Therefore, 1.25 mmol KOH was selected for the subsequent study. The yield of DMC was 20% in the 2nd run (Table 8, entry 6) and decreased slightly to 18% in the 3rd run (Table 8, entry 7). Therefore, DBU is practically reusable from the above results.

### 3.10 The scale-up experiment





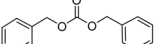
The reaction was scaled up under the conditions of oil bath temperature 60 °C, initial pressure 0.25 MPa and reaction time 12 h. The specific steps are as follows: a mixture of 15.0 mmol CH<sub>3</sub>OH, 15.0 mmol **IL**, 22.5 mmol DBU, 45.0 mmol CH<sub>2</sub>Br<sub>2</sub> and 4.5 mL CH<sub>3</sub>CN was added in a 75 mL stainless-steel autoclave, then CO<sub>2</sub> was charged to the autoclave up to 0.25 MPa at room temperature. After that, the autoclave was placed in an oil bath preheated to 60 °C. After stirred for 12 h, the autoclave was cooled down to room temperature. The yield of DMC is 79% analyzed by GC using biphenyl as an internal standard. The scale-up experiment for direct synthesis of DMC under balloon pressure without **IL** was also carried out with a GC yield of 22% in 2 h.

### 3.11 Substrate scope in carbonate synthesis

We further studied the substrate scope in carbonate synthesis using different alcohols under the conditions as follows: oil bath temperature 60 °C, initial pressure 0.25 MPa, reaction time 12 h, alcohol 1.0 mmol, **IL** 1.0 mmol, CH<sub>2</sub>Br<sub>2</sub> 3.0 mmol, DBU 1.5 mmol and 0.3 mL acetonitrile. The reaction of CO<sub>2</sub> with ethanol, 1-butanol or benzyl alcohol has been investigated and the results are shown in Table 9. It is clear that the yields of the corresponding carbonates are 80%, 82% and 79%, respectively.



Table 9 Substrate scope in carbonate synthesis<sup>a</sup>

Entry	Alcohol	Product	Yield <sup>b</sup> (%)
1	CH <sub>3</sub> OH		81
2	CH <sub>3</sub> CH <sub>2</sub> OH		80
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH		82
4			79

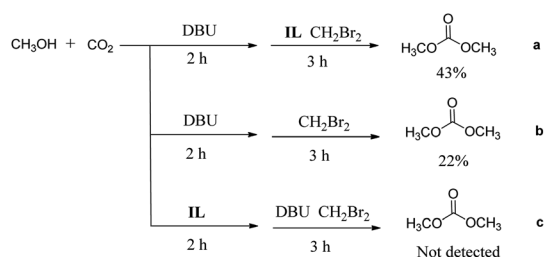
<sup>a</sup> Reaction conditions: alcohol 1.0 mmol, DBU 1.5 mmol, **II** 1.0 mmol, CH<sub>3</sub>CN 0.3 mL, CH<sub>2</sub>Br<sub>2</sub> 3.0 mmol, CO<sub>2</sub> initial pressure 0.25 MPa, 60 °C, 12 h. <sup>b</sup> Yield of carbonate determined by GC using an internal standard technique.

### 3.12 The reactant control experiments

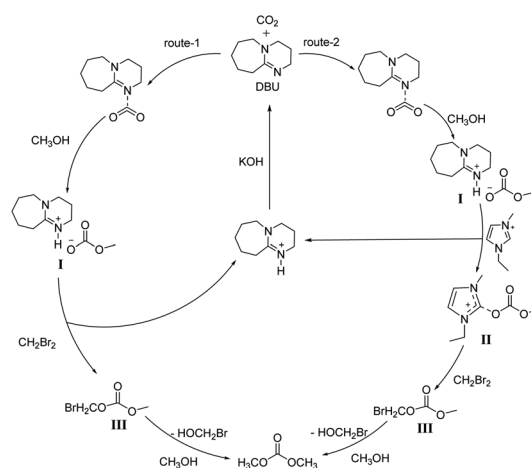
To explore the possible reaction mechanism, a series of substrate control experiments have been carried out and the results are shown in Scheme 1. Taking the process a as an example, the experimental steps are as follows: an appropriate amount of CO<sub>2</sub> was charged to a 25 mL autoclave containing a mixture of 1.5 mmol DBU, 1.0 mmol methanol, and 0.3 mL CH<sub>3</sub>CN at room temperature, the autoclave was placed in an oil bath preheated to 60 °C. After stirred for 2 h, the autoclave was cooled down to room temperature, and the remaining CO<sub>2</sub> was removed slowly. 1.0 mmol **II** and 3.0 mmol CH<sub>2</sub>Br<sub>2</sub> were added to the autoclave, then the autoclave was placed in the oil bath again. After stirred for 3 h, the autoclave was cooled down to room temperature. Gas chromatography was used to analyze the yield of DMC through a standard curve. It can be seen that the yield of DMC in the process a was 43%. The DMC yield was 22% in process b without **II**. Whereas in process c, **II** was added in the initial step and no product was observed in the subsequent reaction step. The results indicate that the reactive intermediate should be [DBUH]<sup>+</sup>[CH<sub>3</sub>OCOO]<sup>-</sup>,<sup>35–38</sup> and **II** acts as a promoter to react with this intermediate to increase the yield of DMC.

### 3.13 Proposed reaction mechanism

After the reaction, the reaction mixture was concentrated under reduced pressure and the reacted DBU and **II** were isolated by



Scheme 1 The reactant control experiments.



Scheme 2 Proposed mechanism for the direct synthesis of DMC.

column chromatography. The isolated DBU and **II** were characterized by <sup>1</sup>H NMR and HRMS (see Fig. S6–S13 in the ESI†). From these spectra, it can be inferred that mixed salts of protonated DBU, hexafluorophosphate anion, and bromide anion were formed after the reaction. Meanwhile, a part of **II** was combined a group with a molecular weight of 31 during the reaction. According to the previously reported,<sup>34–40</sup> as well as the results in this study, two plausible mechanism routes for direct synthesis of DMC have been proposed and shown in Scheme 2. The route-1 is that DBU combines with CO<sub>2</sub> to form a DBU-CO<sub>2</sub> adduct. Subsequently, the adduct is alcoholized by the nucleophilic attack of the O atom on the methanol, and the H atom of the hydroxyl group is transferred to the N atom of the DBU to form an amidinium alkyl carbonate intermediate **I** [DBUH]<sup>+</sup>[CH<sub>3</sub>OCOO]<sup>-</sup>. Intermediate **I** forms protonated DBU and intermediate **III** after being attacked by CH<sub>2</sub>Br<sub>2</sub>. The characteristic peak of intermediate **III** ([M + H]<sup>+</sup> 170.81) was detected in the mass spectra of the reaction mixture (see Fig. S14 in the ESI†). Finally, intermediate **III** is attacked by the nucleophile methanol to form the final product DMC. Besides, DBU is proved to be recyclable after having been treated with KOH in ethanol.

Intermediate **I** is formed firstly in the route-2. Then the carbon atom between the two nitrogen atoms of the imidazole cation in the **II** combines with the oxygen ion in intermediate **I** to produce an intermediate **II**. This unstable intermediate is attacked by CH<sub>2</sub>Br<sub>2</sub> to form intermediate **III**, then the target product DMC is generated. In view of the fact that **II** can promote the production of DMC to increase the yield, we consider that the reaction undergoes both route-1 and route-2 in the presence of **II**, while the reaction undergoes route-1 in the absence of **II**.

## 4. Conclusions

In summary, a mild and efficient protocol for direct synthesis of DMC from CO<sub>2</sub> and methanol under low initial pressure was developed in the presence of CH<sub>2</sub>Br<sub>2</sub>, DBU, and **II**s. The



reaction conditions were systematically investigated and the optimal conditions were obtained as follows: oil bath temperature 60 °C, initial pressure 0.25 MPa, reaction time 12 h, methanol 1.0 mmol, 1.0 equiv 1-ethyl-3-methylimidazole hexafluorophosphate, 3.0 equiv CH<sub>2</sub>Br<sub>2</sub>, 1.5 equiv DBU and 0.3 mL acetonitrile, resulting in an 81% yield of DMC. The reaction can be carried out under balloon pressure using CH<sub>2</sub>Br<sub>2</sub>, DBU with or without **II**, providing the DMC yields of 62% (12 h) and 23% (2 h), respectively. DBU is proved to be recyclable in the absence of **II**.

## Conflicts of interest

There are no conflicts to declare.

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