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Introduction

The development of environmentally benign chemicals and synthetic methods is a challenging field in green chemistry.¹ As important green organic intermediates, unsymmetrical and symmetric organic carbonates play essential roles in the chemical industry.^{2,3} For example, ethyl methyl carbonate (EMC) as the simplest unsymmetrical carbonate, is widely applied in methylation, ethylization and methoxycarbonylation reactions.⁴ Moreover, it can act as an established solvent, as a useful protecting group of alcohols and phenols,⁵ and as a co-solvent in a non-aqueous electrolyte of lithium ion cells.^{6,7}

In general, the synthesis of EMC is divided into three categories.⁸ A traditional way to produce EMC is the esterification of methyl chloroformate with alcohol catalyzed by base catalysts,⁹ but this route is widely considered not environmentally benign since the reagents used are highly toxic. Another method is the oxidative carbonylation of CO, O₂, methanol and ethanol,

CO₂ promoted synthesis of unsymmetrical organic carbonate using switchable agents based on DBU and alcohols[†]

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1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is an effective nucleophilic catalyst for the transesterification of dimethyl carbonate (DMC) with various alcohols and amines, which afforded unsymmetrical organic carbonate and carbamate. It was observed that the transesterification was accelerated under pressurized CO_2 in this work. The activity is very high and the best result (89% conversion with 98% selectivity to unsymmetrical carbonate) was obtained for the DBU/alcohol/DMC/CO₂ system. The addition of CO_2 to DBU/ethanol generated the DBU cation salt, [DBUH][OCOOCH₂CH₃], which dissociated more favorably under increasing reaction temperature even under pressurized CO_2 . The salt could also help to activate DMC by H-bond interaction. The reaction system can be extended easily for the catalytic synthesis of carbamates from amines and DMC. After the reaction, the salt was separated from the reaction mixture and DBU can be recovered by the feasible thermal decomposition, offering a straightforward strategy for the recycling of DBU. On the basis of these results, a plausible mechanism involving the role of both DBU and CO_2 has been proposed.

which has drawbacks such as low productivity of EMC and easy production of by-products.^{10,11} Except for the above two methods, EMC can also be prepared by the transesterification of dimethyl carbonate (DMC) with diethyl carbonate (DEC) or DMC with ethanol. The transesterification of DMC with DEC can be catalyzed using MgAl₂O₄ composites,¹² carbon-supported MgO,¹³ metal-organic frameworks (MOFs),¹⁴ zeolitic imidazole frameworks (ZIF-8, ZIF-67),^{15,16} carbonate phosphonium salts etc.¹⁷ However, this route suffers from low production efficiency, poor yields of EMC and poor atom economy. For the transesterification of DMC with ethanol to synthesize EMC, heterogeneous catalysts such as molecular sieves (4 Å) and TiO_2 nanofibers were discovered to be effective.^{18,19} Among homogeneous catalysts, metal complex $Co_2(CO)_8$ showed appreciable catalytic activity in the reaction of DMC with primary alcohols and gave alkyl methyl ethers with high selectivity and high yields (95-98%).²⁰ Unfortunately, the high reaction temperature (180 °C) and the sensitivity of Co₂(CO)₈ to air limited the practical application of the system. In another study, stoichiometric Brønsted acid catalysts p-toluenesulfonic acid or H₂SO₄ and Lewis acid catalysts AlCl3 or FeCl3 have been used in the reaction of alcohols or phenols with DMC, but a long reaction time could be necessary to afford good conversion and selectivity.²¹ Thus, more research of the transesterification of DMC with alcohols has been focused on base catalysts. For example, both 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can be applied as homogeneous basic catalysts for the production of alkyl/aliphatic

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 $[\]dagger$ Electronic supplementary information (ESI) available: The pK_b values of different bases; the observation of phase behavior; ¹H NMR spectra of the equimolar mixture of DBU/methanol and DBU/ethanol before and after bubbling CO₂; ¹³C NMR spectrum of [DBUH][O(CO)OCH₂CH₃]; the conductivity of DBU, ethanol and their mixture; ¹H NMR, ¹³C NMR spectra, FT-IR data and ESI-MS data of all isolated products. See DOI: 10.1039/c8nj01638k

Paper

methyl carbonates and polycarbonates from alcohols/diols and DMC.^{5,22} MCM-41-TBD and polystyrene-supported DBU have been established to solve the difficult catalyst-product separation of homogeneous basic catalysts like TBD/DBU in reaction mixtures, but the immobilization of a guanidine/amidine base onto an inorganic siliceous mesoporous support by a covalent bond is normally needed.²³⁻²⁵ Moreover, the transesterification reactions catalyzed by them commonly need higher reaction temperatures and longer reaction times (Table S1, ESI⁺). An alternative and more efficient separation method is to take advantage of the switchable property of the CO₂/superbase system.²⁶ It had been reported that TBD was separated readily from a homogeneous mixture by bubbling CO₂ into the reaction mixture at the end of the aldol condensation reaction.²⁷ TBD can be reused for the consecutive catalytic recycles. Moreover, the switchable CO₂/superbase system could work even in the presence of alcohols.²⁸ The existence of CO₂ can help the separation of the superbase in a simple way in the alcohol/CO2 system by forming a [base-H][O(CO)OR] salt when bubbling acid gas (CO₂) through an equimolar mixture of a superbase and an alcohol.²⁹⁻³¹ Furthermore, the ionic product can be converted back to the superbase and the alcohol by vacuumizing, heating or bubbling N₂ through the ionic compound.³²

In this work, we have performed the transesterification of DMC with ethanol by using DBU as a catalyst. Most interestingly, we found that the introduction of CO_2 into DBU/ethanol/DMC at the beginning of the reaction enhanced the catalytic activity significantly when the reaction temperature was above 90 °C. Moreover, this demonstrated that DBU/ethanol/CO₂ can act as a switchable catalyst, which existed in the form of solid and had poor solubility in nonpolar solvents after the reaction, and thus allowed the recycling of DBU under pressurized CO_2 . The present approach has the advantages of excellent catalytic activity, easy separation and benign to the environment.

Experimental section

Chemical materials

All chemicals were analytical grade and commercially available. The organic base, 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), was purchased from Aladdin Bio-Chem Technology Co., Ltd, and directly used as received. Dimethyl carbonate (DMC) was purchased from Adamas Reagent Co., Ltd, and was also used without further purification. Ethanol and toluene were both purchased from Shanghai Titan Scientific Co., Ltd, and dried by using standard methods. All other kinds of alcohols and amines such as *n*-propanol, *i*-propanol, *n*-butanol, *t*-butanol, *n*-hexanol, benzyl alcohol, ethylene glycol, furfuryl alcohol, 4-pyridinemethanol, *n*-propylamine, *i*-propylamine and *n*-butylamine were purchased from Sinopharm Chemical Reagent Co., Ltd and were also used without further purification. CO₂ (>99.95%) and N₂ (>99.999%) were supplied by Shanghai Weichuang Gas Factory.

Characterization

Room temperature ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 MHz instrument (400 MHz ¹H NMR, 100 MHz ¹³C NMR). High temperature ¹H NMR spectra were recorded on a Bruker AVANCE 500 MHz instrument (500 MHz ¹H NMR). FT-IR spectra were recorded at room temperature on a Magna 550 (Nicolet, USA) FT-IR spectrometer. A spectrum of dry KBr was also recorded as the background. Mass spectra were recorded on a Xevo G2 TOF spectrometer in the electrospray positive ion mode (ESI†). The phase behavior was directly observed during the whole reaction process by using a high pressure autoclave equipped with transparent glasses on opposite sides (Fig. S1, ESI†). The conductivity of the liquid was measured using a Leici DDS-307 conductivity meter according to the previously reported procedure.^{33,34}

Transesterification reaction between DMC and ethanol

The transesterification reaction of dimethyl carbonate (DMC) and ethanol to ethyl methyl carbonate (EMC) was used as a model reaction to evaluate the catalytic performance. The catalyst DBU (5 mmol), ethanol (5 mmol), DMC (15 mmol) and toluene (3 mL) were added into a Teflon bush, and then the bush was put into a 50 mL stainless steel autoclave (a working capacity of approximately 40 mL) and sealed. The autoclave was purged with dry CO₂ three times to remove the air, and charged with CO2 to the desired pressure. Finally, the reactor was heated in a temperature-controlled heating jacket to the desired temperature. After the reaction, the reactor was immediately cooled in an ice-water bath, and CO2 was slowly released while extra anhydrous toluene at 10 °C was employed to absorb the trace amounts of DMC and the products entrained by CO₂. After depressurization, the anhydrous toluene in the cold trap was added to the reactor to wash off the absorbed substances on the wall, and then the mixture in the reactor was transferred to a 25 mL vessel. Anhydrous ethyl ether was added to the reaction mixture to promote catalyst separation. The white solid was separated by standing and filtration, and the filtrate was analyzed by GC and GC-MS analysis. The white solid ([DBUH][O(CO)OR]) was further washed with ethyl ether two times and dried under vacuum at 50 °C to remove the alcohol and CO₂. The left DBU can be reused directly in the next reaction. Various carbonates and carbamates were synthesized by the transesterification reaction of DMC with corresponding alcohols and amines according to a procedure similar to that mentioned above. The reaction products were analyzed by gas chromatography on a Shimadzu GC-2014 apparatus equipped with a KB-50 column (30 m imes 0.32 mm imes 0.50 μ m) and an FID detector. GC-MS analyses were conducted on an Agilent-6890/GC-5973 MS instrument with a HP-5 column (30 m imes 0.25 mm imes 0.25 μ m). The products were also isolated by silica gel column chromatography and analyzed by ¹H NMR spectroscopy (as shown in the ESI[†]).

Results and discussion

Catalytic performance

The organic superbase can effectively catalyze transesterification between the alcohol and dimethyl carbonate (Scheme 1). As a typical example, the reaction of DMC with ethanol could afford two products; EMC and diethyl carbonate (DEC).³⁵



Scheme 1 Synthesis of unsymmetrical organic carbonate from DMC and alcohol.



Fig. 1 Conversions of ethanol and selectivities to DEC over different base catalysts. Reaction conditions: DBU 0.76 mL (5 mmol), ethanol 0.29 mL (5 mmol), DMC 1.26 mL (15 mmol), toluene 3 mL 90 °C, 6 h.

Firstly, different basic catalysts were evaluated for the transesterification of DMC with ethanol to synthesize EMC, and the results were summarized in Fig. 1. It was observed that triethylamine (Et₃N), 1,1,3,3-tetramethylguanidine (TMG) and K₂CO₃ only exhibited low activity although these bases afforded high selectivity to EMC. When DBU and TBD were used as the base catalysts, the conversion of ethanol was 77.2% and 92.8%, respectively. However, DBU afforded much higher selectivity to EMC (98.7%) while TBD could only afford moderate selectivity to EMC (<90%). The catalytic activity of these various basic catalysts was found to be in the following order: TBD > KOH > DBU > K_2CO_3 > TMG \approx Et₃N. Interestingly, the catalytic activity order was partly consistent with the basicity order of different bases (Table S2, ESI^{\dagger}),^{36,37} that is, TBD > KOH > $DBU > TMG > Et_3N > K_2CO_3$. Expect for TMG and K_2CO_3 , the smaller the $pK_{\rm b}$ value of the basic catalysts, the higher the catalytic activity achieved. It indicated that the stronger basicity of the catalysts enables the reaction within a certain basic range.

On the basis of the results above, one of the advantages of using DBU as the catalyst is that DBU shows excellent catalytic performance and could be recycled in the form of an ionic compound because the ionic compound has poor solubility in weak polar solvents, such as toluene. It should be noted that although KOH exhibited high conversion (88%) and selectivity (90%), the separation is difficult and large amounts of residues are generated after the reaction.³⁸ Moreover, DBU is also much cheaper than TBD. Hence, among all these basic catalysts, DBU was chosen as a catalyst in the following investigation owing to its excellent catalytic performance, low cost and potential recyclability.

DBU can form an ionic product in the presence of alcohol and CO₂, which could favor DBU separation. Normally, DBU could be separated by CO₂ bubbling into the solution after reaction. However, the effect of CO_2 on the transesterification reaction has rarely been considered. In this work, we observed that the addition of CO_2 to the reaction system produced an important impact on the reaction. Initially, the effects of reaction conditions (temperature, CO₂ pressure and reaction time) on the catalytic activity were investigated by using DBU as a catalyst. As shown in Fig. 2a, the reaction temperature had a significant effect on the reaction. With an increase in the temperature from 60 °C to 100 °C, the conversion of ethanol increased apparently from 9% to 89%, and the conversion increased slowly to 91% at 110 °C. The higher temperature might result in the decomposition of DBU. Consequently, it was suggested that 100 °C was the appropriate temperature for the transesterification reaction. The influence of the reaction time is shown in Fig. 2b. Under the conditions of 100 °C and 1.0 MPa, the conversion of ethanol had a gradual increase from 1 h to 6 h and then remained almost unchanged with high selectivity from 6 to 8 h, which could be assigned to the reaction equilibrium.

Sequentially, the impact of CO₂ pressure on the transesterification reaction of DMC was examined and depicted in Fig. 2c. It is noteworthy that the conversion of ethanol was increased obviously as the CO_2 pressure was increased to 1.0 MPa. However, the conversion of ethanol had a slight decrease while selectivity showed no obvious changes at a higher pressure range. The enhancement of the catalytic activity by increasing CO₂ pressure might be due to the formation of an intermediate product during the reaction. [DBUH][O(CO)OCH2CH3] is normally considered as an intermediate resulting from DBU, ethanol and CO₂ (Scheme 2). The initial increase in the conversion of ethanol could possibly be explained due to the fact that the introduction of CO₂ can result in consumption of ethanol to form [DBUH][O(CO)OCH₂CH₃], which could act as a catalyst precursor and facilitate the formation of EMC. However, as CO₂ pressure was higher than 1.0 MPa, more CO2 dissolved in toluene, which could capture too much DBU to form the catalyst precursor [DBUH][O(CO)OCH2CH3] with ethanol, resulting in a more difficult dissociation of the precursor into the active species (see the following discussion). This might be also related to a dilution effect whereby the excess CO2 reduced the concentration of DMC in the vicinity of the catalyst.

In order to identify further the effect of CO_2 on the catalytic transesterification between ethanol and DMC, the conversion/time curves of the transesterification under different CO_2 pressures were plotted and shown in Fig. 3. It was indicated that the conversions of ethanol under CO_2 pressures of 0.5 MPa, 1.0 MPa and 1.8 MPa were all higher than that without CO_2 , and the highest activity was obtained under a CO_2 pressure of 1.0 MPa. This result revealed that the introduction of CO_2 indeed facilitated the transesterification reaction of DMC in the DBU/ethanol system.

Next, the dependence of ethanol conversions on the reaction temperature has been examined in the presence or absence of CO_2 , respectively. As shown in Fig. 4, the catalytic activity increased with the reaction temperature either without CO_2



Fig. 2 Effects of reaction parameters on ethanol conversion for transesterification. Reaction conditions: DBU 0.76 mL (5 mmol), ethanol 0.29 mL (5 mmol), DMC 1.26 mL (15 mmol); toluene 3 mL. (a) Time 5 h, CO₂ pressure 1.0 MPa, (b) temperature 100 °C, CO₂ pressure 1.0 MPa, (c) temperature 100 °C, time 8 h. The selectivity to EMC was always close to 98%.



Scheme 2 Reversible reaction between CO₂ and DBU in ethanol.

or with CO_2 in the reaction system. However, the addition of CO_2 had a negative effect on the transesterification reaction between DMC and ethanol when the reaction temperature was lower than 80 °C. In contrast, CO_2 facilitated the reaction significantly when the reaction temperature was over 90 °C, as compared with that without CO_2 (Fig. 4). These results demonstrated that as the reaction temperature was increased under pressurized CO_2 , the transesterification reaction might





Fig. 3 Ethanol conversion as a function of reaction time under different CO_2 pressures for the transesterification reaction. Reaction conditions: DBU 0.76 mL (5 mmol), ethanol 0.29 mL (5 mmol), DMC 1.26 mL (15 mmol), toluene 3 mL, 100 °C. (a) Without CO_2 , (b) under 0.5 MPa CO_2 , (c) under 1.0 MPa CO_2 , (d) under 1.8 MPa CO_2 . The selectivity to EMC was always close to 98%.

Fig. 4 Conversions of ethanol at different temperatures in the presence or absence of CO_2 . Reaction conditions: time 4 h, DBU 0.76 mL (5 mmol), ethanol 0.29 mL (5 mmol), DMC 1.26 mL (15 mmol), toluene 3 mL. The selectivity to EMC was always close to 99%.

follow a different approach resulting from the mutual-interaction among CO₂, DBU and ethanol, which might be dependent on the reaction temperature.

Phase behavior

The mutual-interaction among CO₂, DBU and ethanol can be reflected directly by observing visually the phase behavior under pressurized CO₂. It was observed that the white solid formed immediately at room temperature even if CO₂ was bubbled into the mixture of ethanol and DBU dissolved in toluene. To clarify further the phase behavior of the reaction mixture during the whole reaction process, a high-pressure visual autoclave equipped with transparent glasses was employed (Fig. S1, ESI†).³⁹ Fig. S2 (ESI†) shows the visual observations of phase behavior as the temperature ranged from 25 °C to 90 °C. The reaction mixture includes three phases of gas (CO₂), liquid (toluene and substrates), and a white solid at low temperatures (\geq 90 °C).

As shown in Fig. S2 (ESI⁺), DBU, DMC, ethanol and toluene were miscible and the solution is transparent at room temperature (Fig. S2a, ESI[†]). After the steel reactor was purged three times with 0.1 MPa CO_2 and then charged with CO_2 up to 0.5 MPa at 25 °C, the white solid formed at the bottom of the glass tube and a liquid phase co-existed (Fig. S2b, ESI[†]). The white solid formed is believed to be [DBUH][O(CO)OCH2CH3] (for identification, see the next paragraph), which had a limited solubility in the presence of a large of amount of toluene. It can be seen that the ionic product was accumulated mostly at the bottom of the liquid phase when the temperature was up to 50–70 °C and the CO₂ pressure remained at 0.5 MPa (Fig. S2c and d, ESI⁺). However, when the temperature was increased to 90 °C, the white solid almost disappeared and the homogeneous liquid phase became transparent (Fig. S2e, ESI⁺). As the CO₂ pressure reached up to 3.0 MPa at 90 °C, a biphasic system consisting of vapor and a transparent liquid can be still observed (Fig. S2e-h, ESI⁺). Nevertheless, after the reaction mixture was cooled to 25 °C and depressurized, the white solid formed again and was accumulated again at the bottom of the liner (Fig. S2i, ESI[†]). At the same time, the liquid level decreased due to the release of CO₂. From the visual observation under reaction conditions, it is very clear that the present transesterification reaction occurred under the gas-liquid biphasic condition. The results indicated that the ionic compound ([DBUH][O(CO)OCH2CH3]) was formed preferentially at a lower temperature, while it could undergo a structure transformation under higher temperatures and thus displayed good solubility.

Transformation of DBU in the course of transesterification reaction

In order to identify the structure of the white solid, as observed previously (Fig. S2, ESI[†]), the white solid was isolated carefully at different reaction times and then characterized by using the FT-IR spectra and ¹H NMR spectra. As shown in Fig. 5a–c (top), two bands at 1107 cm⁻¹ and 1207 cm⁻¹ could be due to the symmetric and unsymmetrical C–O–C stretching vibrations. There also appears a strong absorption at 1647 cm⁻¹ and a weak peak at 1324 cm⁻¹ which belong to C=O and C–O of the (O=C–O–)–R group stretching absorption bands, respectively.³⁰



Fig. 5 After different reaction times, the as-obtained white solid was analyzed using the FT-IR spectra (top) and ¹H NMR spectra (bottom). Reaction conditions: temperature 100 °C, CO₂ pressure 1.0 MPa, 5 mmol DMC, 5 mmol DBU, 5 mmol ethanol, 3 mL toluene were added, respectively. (a) Reaction 3 h, (b) reaction 5 h, (c) reaction 8 h, (d) the isolated white solid was dried at 60 °C for 1 h, (e) DBU. The chemical shift appeared at δ = 3.79 was attributed to the proton from residual DMC.

The existence of the C–O–C group and the (O=C–O–)–R group confirmed the anion moiety of the ionic compound. The N–H stretching of the separated solids at 3117 cm⁻¹ and 3240 cm⁻¹ indicated the DBU protonation.⁴⁰ The weak absorption at 1590 cm⁻¹ is associated to the ν (C=N) group of the DBU ring. In addition, the bands at 2859 cm⁻¹ and 2935 cm⁻¹ were due to the C–H stretching vibration in the ring and from the alcohol.⁴¹ The FT-IR spectra of all the separated solids gave a broad spectral response at ~3382 cm⁻¹ due to the trace water in the thin KBr disk prepared under an air atmosphere.

For the sake of comparison, the white solid was isolated, and then further dried at 50 °C under vacuum to obtain a colorless liquid, which was then characterized by FT-IR and ¹H NMR as well (Fig. 5d, top). The as-obtained liquid showed a peak at 1613 cm⁻¹, which is attributed to the C—N ring stretching vibration of the DBU ring. Meanwhile, two peaks that appeared at 2925 cm⁻¹ and 2850 cm⁻¹ correspond to the C–H stretching vibration of the DBU ring as well (Fig. 5d and e, top). Actually, both pure DBU (Fig. 5e) and the as-obtained liquid showed very similar vibrations in the FT-IR spectra, which means that [DBUH][O(CO)OR] generated DBU owing to thermal decomposition, alcohol and CO₂. The latter two contents are removed while the DBU was left, providing an attractive approach for the recycling of DBU.

The ¹H NMR spectra of the isolated white solids are also shown in Fig. 5a-c (bottom). Obviously, the ¹H NMR signals of all hydrogen protons on the DBU ring shifted to high field as the reaction time extended, even the H6 proton shifted more obviously, from 2.61 to 2.50 (Fig. 5a-c), which might be related to the formation of more [DBUH][O(CO)OCH₃] (the equation shown in Fig. 5). This was consistent with the results shown in Fig. S3 and S4 (ESI⁺), the H2-6, H9-11 protons from [DBUH][O(CO)OCH3] indeed gave signals at higher field (Fig. S3, ESI⁺), as compared with the protons from [DBUH][O(CO)OCH2CH3] (Fig. S4, ESI[†]). Compared to the spectra of pure DBU (Fig. 5e, bottom), the ionic products showed a chemical shift towards lower field, and the hydrogen protons (H2,6,9,11) that were close to the functional group of N-H showed a larger shift (Fig. 5a–c vs. Fig. 5e). The two new peaks observed at δ = 3.99 and δ = 3.58 were assigned to the H13 proton and the H15 proton in $[O(CO)OCH_2CH_3]^+$ and $[O(CO)OCH_3]^+$, respectively when the reaction time was 3 h. It was found that the ratio of H13/H15 gradually decreased with prolonged reaction time from 3 h to 5 h, and even the peak of the H13 proton was hardly observed after 8 h. This means that the amount of [DBUH][O(CO)OCH₂CH₃] in the white precipitate decreased while the amount of [DBUH]-[O(CO)OCH₃] gradually increased with the reaction time. This phenomenon was consistent with the fact that the consuming ethanol reacted with DMC to afford EMC and the by-product MeOH. In addition, the ¹³C NMR spectra of the white solid as observed in the phase behavior have been measured when CO₂ was purged into the tube (Fig. S2, ESI⁺). As shown in Fig. S5 (ESI⁺), three peaks observed at δ = 159.71, δ = 60.44 and δ = 15.81 were assigned to C12, C13 and C14 in the anion moiety of the ionic compound, respectively.⁴² This result proved that the white solid was a DBU-based salt, which resulted from the reaction of DBU, CO₂, and ethanol, being consistent with that of the ¹H NMR spectra.

The other new peak that appeared at $\delta = 1.21-1.25$ could be attributed to the H14 proton of the $-CH_3$ in the anion part of the ionic compound (Fig. 5). Along with all other peaks, the new peaks demonstrated the formation of the ionic product ([DBUH][O(CO)OCH₃]). Moreover, once the isolated solid was dried under vacuum, the resulting liquid showed a very similar ¹H NMR spectrum to that of DBU, which was highly consistent with the FT-IR data and provided further verification on the recyclability of DBU. Thus, the combination of FT-IR and ¹H NMR analysis clearly showed that CO₂, DBU and ethanol can form the ionic product [DBUH][O(CO)OCH₂CH₃], which is further converted into [DBUH][O(CO)OCH₃] as the transesterification reaction proceeds. [DBUH][O(CO)OCH₃] can be separated and dried by simple drying, allowing for the effective recycling of DBU.

Considering that the reaction of DBU, ethanol and CO₂ to produce [DBUH][O(CO)OCH₂CH₃] is an exothermic reaction, the formation of the intermediate species [DBUH][O(CO)OCH₂CH₃] was not favorable under increasing temperature conditions. As shown in Fig. 6 (top), the ¹H NMR spectra of the reaction mixture were recorded over the temperature range of 25–55 °C. Equimolar DBU and ethanol was added dropwise to an NMR tube under a N₂ atmosphere at room temperature. CO₂ was bubbled in the solution for 30 min at a required test temperature, and then the tube was capped and sealed with Teflon tape and reserved in a heat preservation cup. It can be seen that the protons H3,5,10 and H2,9,11 moved to high field and even H6 close to the functional group of N–H showed more obvious tendency with increasing temperature, revealing the possible changes of the DBU cation salts. The peaks at $\delta = 1.25$ assigned to the overlay of H14 and H14′



Fig. 6 ¹H NMR spectra of the mixture of DBU and ethanol after CO₂ was bubbled through the solution at different temperatures (a) 25 °C, (b) 35 °C, (c) 45 °C, (d) 55 °C using internal CDCl₃ as a chemical shift reference (top). The molar ratio of DBU/[DBUH]⁺ was determined from the ¹H NMR spectra and found to change with temperature (bottom).

in the $-CH_3$ of ethanol and $[O(CO)OCH_2CH_3]^+$ were indistinguishable. However, the H13' and H13 in the -CH2 of unconverted ethanol and [O(CO)OCH2CH3]⁺ displayed a totally different resonance signal and appeared at $\delta = 3.67$ and δ = 3.97, respectively. It could be clearly seen that the intensity of the peak at δ = 3.97 decreased while the intensity of the peak at δ = 3.67 increased when the test temperature was increased, which revealed that the amount of [DBUH][O(CO)OCH₂CH₂] decreased while the amount of ethanol increased when the temperature was increased from 25 °C to 55 °C. Accordingly, the molar ratio of DBU to [DBUH]⁺ was derived from the ¹H NMR peak area, and the effect of temperature on the ratio of DBU/ [DBUH]⁺ is shown in Fig. 6 (bottom). We could see that the ratio of DBU/[DBUH]⁺ increased with an increase in the temperature and the improvement of the amount of DBU was enormous when the temperature was increased from 45 °C to 55 °C. As previously reported by Xie et al. as well as Phan et al., the decomposition onset temperature of a DBU-based ionic compound is around 50-60 °C.40,43 Thus, the concentration decrease of [DBUH][O(CO)OCH2CH3] with increasing temperature was attributed to the reverse reaction caused by the thermal decomposition of the ionic compound. Although the molar ratio of DBU/[DBUH]⁺ at the reaction temperature (90–100 °C) and a high pressure (1.0 MPa) cannot be determined from NMR measurement, more dissociation of this ionic compound into DBU was highly believable. The results were also in good agreement with the phase behavior shown in Fig. S2 (ESI†), in which the ionic product was not soluble and existed as a white solid at low temperature in toluene, while DBU and ethanol originated from the dissociation of the DBU salt were miscible with toluene and thus remained in an almost homogeneous phase with increasing temperature.

Considering the formation of ionic compounds under pressurized CO₂, the conductivity of the mixed DBU/ethanol system was subsequently measured under different CO₂ pressures. A mixture of DBU (5.5 mL) and ethanol (6.1 mL) was added to the steel reactor for conductivity measurement. Excess ethanol $(n_{\text{ethanol}}/n_{\text{DBU}} = 3)$ was added to increase the solubility of [DBUH][O(CO)OCH₂CH₃], which allowed for a homogeneous phase and to ensure the accuracy of the test. As shown in Fig. 7, the conductivity was recorded after the temperature reached equilibrium for 2 h at 40 °C. The conductivity of the mixture of DBU and ethanol is very low (90.8 μ s cm⁻¹). However, after the steel reactor was purged three times with 0.1 MPa CO₂, the ionic compound [DBUH][O(CO)OCH2CH3] formed in ethanol exhibited a high conductivity of *ca.* 2040 μ s cm⁻¹. Then, the conductivity of DBU/ethanol/CO2 gradually increased with an increase in the CO₂ pressure and maximized at 3620 μ s cm⁻¹ under the condition of 0.9 MPa CO₂. The results indicated the ionic change of the system and revealed the formation of the salt [DBUH][O(CO)OCH2CH3]. However, the conductivity of DBU/ethanol/CO2 showed a slight decrease when the CO2 pressure continued to increase to 1.1 MPa or a higher pressure. It could possibly be explained that more CO_2 can be dissolved in ethanol with increasing pressure, resulting in the reduced polarity of the solution as well as the produced diluting effect.



Fig. 7 Conductivity of the DBU/ethanol/CO₂ system as a function of CO₂ pressure at 40 °C. The conductivity was measured with a mixture of DBU (5.5 mL) and ethanol (6.1 mL).

Reaction mechanism

On the basis of the previous report,⁴⁴ the reaction catalyzed by DBU in the absence of CO_2 could proceed according to the following mechanism:

$$DBU + DMC \rightleftharpoons [DBU-CO(O)CH_3][OCH_3]$$

 $[DBU-CO(O)CH_3][OCH_3] + CH_2CH_3OH \rightleftharpoons EMC + CH_3OH + DBU$

This mechanism is catalytic and is likely to be active because there will always be some free DBU resulting from the decomposition of the DBU-based salts to promote this reaction at slightly high temperatures. However, according to our present results, the addition of CO_2 can facilitate the reaction, which implied that CO_2 might have played a crucial role in the reaction as follows:

 $DBU + CH_3CH_2OH + CO_2 \rightleftharpoons [DBUH][O(CO)OCH_2CH_3]$

 $[DBUH][O(CO)OCH_2CH_3] + DMC \rightleftharpoons EMC + [DBUH][OCH_3] + CO_2$

$$[DBUH][OCH_3] + CO_2 \rightleftharpoons [DBUH][O(CO)OCH_3]$$

In this case, the role of DBU is the activation of CO_2 that might generate an alternative pathway of EMC generation *via* a [DBUH][O(CO)OCH₂CH₃] intermediate as described. To identify the reaction mechanism more clearly, the reaction kinetics was then investigated for the transesterification reaction with the initial rate method. The relationship between the reaction rate (R_0) and the concentrations of DBU is shown in Fig. S6 (ESI[†]). The study showed 1.32-order plots for the concentration of DBU (0.50–1.25 M). This implied that the reaction intermediate step could need more than one molecule of DBU to complete the catalytic cycle. Nevertheless, the first catalytic mechanism cannot be excluded, which likely results in the fractional reaction order. The free DBU and DBU-based salt [DBUH][O(CO)OCH₂CH₃] coexisted in the reaction mixture, which displayed the combined effect of the catalytic and



Scheme 3 Proposed reaction mechanism for the transesterification reaction between DMC and ethanol under pressurized CO_2 .

stoichiometric pathways, resulting in the enhanced activity under pressurized CO₂.

With respect to the results above, a reasonable reaction mechanism is proposed as shown in Scheme 3. Initially, [DBUH][O(CO)OCH₂CH₃] was formed easily from DBU, ethanol and CO₂ at room temperature. However, when the temperature was increased to 90-100 °C, accompanied by the dissociation of the DBU salt and the release of CO₂, the intermediate species DBUH-OEt generated. However, the dissociation reaction of the DBU salt was reversible and this means that the salt [DBUH][O(CO)OCH₂CH₃] and DBUH-OEt might coexist in the present reaction system. Moreover, as shown in Table S3 (ESI⁺), the conductivity of the mixture of DBU and ethanol (the molar ratio of DBU/ethanol is 1:3) was 77.9 µs cm⁻¹, which was much higher than those of both ethanol (4.14 μ s cm⁻¹) and DBU $(2.85 \ \mu s \ cm^{-1})$. The sharp rise in the conductivity of the DBU/ ethanol mixture could be explained by the production of the intermediate species, in which DBU had a tendency to accept a proton from ethanol, resulting in the activation of ethanol as a nucleophile.²⁹ Similar results were reported for reactions between DBU and propanol/benzyl alcohol/glycerol.45-47

In the previously reported reaction mechanism of transesterification, DBU acts as a nucleophile towards a variety of electrophiles, such as DMC, and activate them by generating the cationic intermediate *N*-alkoxycarbonyl DBU derivative [DBU(CO)OCH₃]. Thereafter, it underwent a nucleophilic attack by an alcohol to afford unsymmetrical carbonate (path 1).^{44,48} However, in the present system, a small amount of the DBU-derived cation [DBUH]⁺ could further activate the cationic intermediate [DBU(CO)OCH₃] by hydrogen bonding interactions (path 2). The strong hydrogen bonding interactions have been identified to play a crucial role in activating an ester bond, leading to the formation of the final products,^{41,49,50} and meantime the basicity could not be the only factor determining the activity and selectivity of the transesterification reaction.⁵¹ It should be noted that the high dissociation of the DBU salt was necessary in order to generate the rich intermediate species [DBU(CO)OCH₃] from free DBU. This was the reason why CO₂ can promote the reaction only under a higher reaction temperature. The synergistic activation of DMC by free DBU and a small amount of [DBUH]⁺ would be more favorable for the nucleophilic attack by ethanol to produce DEC. An unprecedented reaction pathway towards acyclic organic carbonate has been reported when [Nb(OEt)5] coupled with 4-dimethylamino-pyridine (DMAP) was used as the catalyst system, where [Nb(OEt)5] functioned as a Lewis acid and as a source of a nucleophilic anion. In this case, two molecules of DMAP are necessary to activate a hemicarbonate intermediate, facilitating the intramolecular nucleophilic attack of the ethoxide group to the C=O bond to afford linear carbonates.⁵² In our experimental observations, no Lewis acid existed but weak Brønsted acid sites [DBUH]⁺ could play a similar role in promoting the nucleophilic attack of the ethoxide group to the C=O bond to afford linear carbonates as shown in Scheme 3. Afterwards, the intermediate species DBUH-OMe was recovered at the same time. Next, the cooled reaction mixture containing DBU, MeOH and CO2 was easily transformed into a large amount of [DBUH][O(CO)OCH₃] and also a small amount of [DBUH][O(CO)OCH2CH3] at the end of the reaction. Finally, the white solid was dried under vacuum and the recovery of DBU was achieved accordingly.

Substrate scope and reusability

The above results demonstrated that DBU, promoted with CO_2 was a highly efficient homogeneous catalyst for the transesterification reaction of DMC and ethanol in toluene. Thus, a series of alcohols were tested to synthesize the corresponding carbonates under optimized reaction conditions to check the scope of the substrates over the present catalytic system and the results are summarized in Table 1. It could be found that the system was applicable to the transesterification reaction of DMC with various terminal alcohols (Table 1, entries 1-4), indicating that a variety of aliphatic alcohols and aromatic alcohols produced the corresponding carbonic esters with high conversions and selectivities within the first 10 h. Ethylene glycol could also react with DMC to produce 1,3-dioxolan-2-one with a conversion of 47.2%. Moreover, the present catalytic system can also be extended to the synthesis of carbamates from amines and DMC, although terminal amines need a longer reaction time to produce the corresponding carbamates (Table 1, entries 7-9), when compared with alcohols. The reactions performed with isopropanol and *t*-butanol (Table 1, entries 10 and 11) showed no product formation during a reaction time of 24 h, likely due to the steric hindrance.¹⁸ When heterocyclic compounds were used as substrates, furfuryl alcohol offered 46.6% conversion but 4-pyridinemethanol gave no reactivity (Table 1, entries 6 and 12). All products were isolated by silica gel column chromatography method and their purity (>98%) was confirmed by ¹H NMR and ¹³C NMR (Fig. S7-S24, ESI[†]).

Table 1	Transesterification reaction betweer	n DMC and alcohol/amine in the	presence of pressurized carbon dioxide ^a
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Entry	Substrates	Products	<i>T</i> (h)	Con. ^{<i>b</i>} (%)	Sel. (%)
1	он	$\sim l_{\circ}$	10	85.5(28.5)	97.0
2	СМ	$\sim \dot{\mu}_{o}$	10	83.1(27.7)	96.2
3	ОН	$\sim \overset{\circ}{\sim} \overset{\circ}{\sim} \sim \sim$	10	79.7(25.6)	99.0
4	ОН		10	65.5(21.8)	99.0
5	ноон	\sim	14	47.2(15.7)	97.8
6	Он	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	22	46.6(15.5)	99.0
7	∧∧№ ₂	∽₀ ^Ů µ∽∽	13	91.8(30.6)	92.5
8	NH ₂	~o ^ℓ _N ↓	13	61.2(20.4)	92.3
9	∧NH₂		13	74.0(24.7)	99.0
10	он	~ Lot	24	0	0
11	OH	~~~~	24	0	0
12	ОН	N N N	24	0	0

^a Reaction conditions: DMC 1.26 mL (15 mmol), alcohols or amines (5 mmol), DBU 0.76 mL (5 mmol), 100 °C, 1.0 MPa CO₂. ^b The conversion was calculated using alcohols and amines. The values in parenthesis refer to DMC conversion.

In the next step, the reusability of the catalyst DBU was examined under the optimal conditions. After the reaction, the catalyst existed in the form of [DBUH][O(CO)OR]. Anhydrous ethyl ether was added to the reaction mixture to help decrease the solubility of [DBUH][O(CO)OR] in the solvent. Then the catalyst was recovered by simple standing and filtration, followed by washing with ethyl ether three times and then dried under vacuum at 50 °C. Subsequently, the recovered DBU can be reused for the next recycle. The reusability of the DBU catalyst is shown in Fig. 8. It indicated that the catalyst could be reusable for at least five times with high product selectivity, although the conversion of ethanol had a slight decrease possibly due to the loss of a trace amount of DBU in the consecutive recycles. It was found that the separation efficiency of the DBU catalyst is 80.2% after five runs, which might be the reason for the loss of catalytic activity.



Fig. 8 Recyclability of DBU. Reaction conditions: DBU 0.76 mL (5 mmol), ethanol 0.29 mL (5 mmol), DMC 1.26 mL (15 mmol), toluene 3 mL, 100 °C, 1.0 MPa CO₂, 8 h.

Conclusions

In summary, DBU has been demonstrated as an effective catalyst for the synthesis of various unsymmetrical carbonates using DMC and corresponding alcohols. A high conversion of alcohols and the excellent selectivity of unsymmetrical carbonate can be achieved under the optimal reaction conditions. It was found that the reaction can be facilitated in the presence of 1.0 MPa of CO_2 through the synergistic activation of DMC by DBU and the cation $[DBUH]^+$ formation under pressurized CO₂, as compared with that without CO₂. Furthermore, the DBU/ alcohol/CO₂ system existed in the solid form after the reaction in toluene, which helps DBU to be easily separated and reused with high activity and selectivity. The present catalytic system can also be extended for the efficient synthesis of carbamates from DMC and amines. Based on the catalytic performance and characterization, we proposed a reasonable mechanism depicting the role of both DBU and CO₂ for this reaction. The results of this work provided an example of the applications of a switchable DBU/alcohol/CO2 system as a metal and halogen ion-free, recyclable and inexpensive catalytic system in organic synthesis and catalysis.

Conflicts of interest

There are no conflicts to declare.

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