Article

Dialkyl Carbonate Synthesis Using Atmospheric Pressure of CO_2

Hiroki Koizumi,* Haruki Nagae, Katsuhiko Takeuchi, Kazuhiro Matsumoto, Norihisa Fukaya, Yoshiaki Inoue, Satoshi Hamura, Takahiro Masuda, and Jun-Chul Choi*

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- ✓ *Low-pressure and low-concentration CO_2 available*
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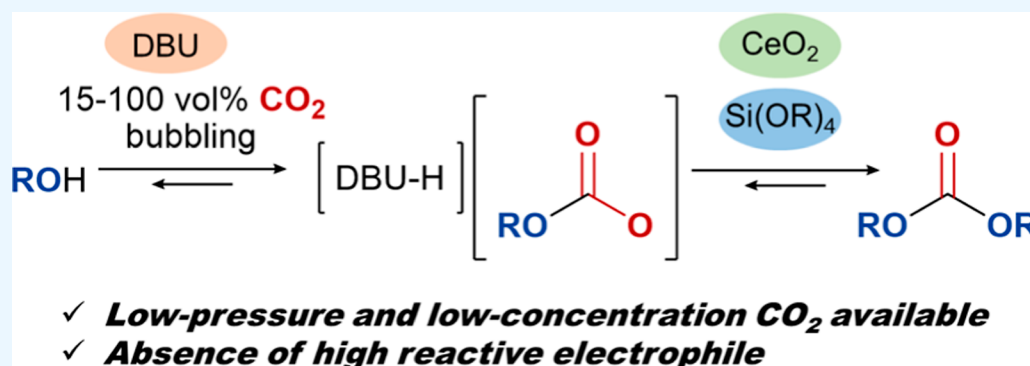
ABSTRACT: Dialkyl carbonates (DRCs) are valuable compounds widely used in the industry. The synthesis of DRC from CO_2 has attracted interest as an alternative to the current method, which uses phosgene. However, the reported approaches for DRC synthesis from CO_2 requires high-pressure and high-concentration CO_2, resulting in elevated costs associated with CO_2 purification and manufacturing facilities. In this report, we present an environmentally friendly method for producing DRC from low-concentration and low-pressure CO_2 via a dehydration condensation approach without the use of halogenated alkylating agents. This method involves the formation of monoalkyl carbonate [BASE-H][ROC(O)O] using a strong organic base and alcohols, tetraalkyl orthosilicates as dehydrating agents, and CeO_2 as the catalyst. Using the method, 39 and 30% of diethyl carbonate yields were accomplished with only 100 and 15 vol % CO_2 (CO_2/N_2 = 15:85) gas bubbling at atmospheric pressure, even under reaction conditions with no large excess of either CO_2, alcohol, or dehydration agent.

INTRODUCTION

Carbon dioxide (CO_2) is widely recognized as the primary driver of global warming as a greenhouse gas, and the use of CO_2 as a C1 source in organic synthesis has emerged as a valuable strategy to simultaneously accomplish carbon recycling and the production of useful chemicals.[1,2] Dialkyl carbonates (DRCs) can be synthesized from CO_2 without a reductive process using hydrogen and are widely used as solvents, electrolytes, fuel additives, and raw materials for polymers.[3,4] In addition, the synthesis of DRC from CO_2 has garnered attention as an environmentally conscious alternative to the current manufacturing method using highly toxic phosgene. However, most of the reported systems for synthesizing DRC from CO_2 require high-pressure and high-purity CO_2, although CO_2 is emitted at low pressure and low concentration from typical emission sources, such as thermal power plants and blast furnace steel mills, and the separation, purification, and compression of the emitted CO_2 to a suitable quality level for use in synthesis involve significant energy and cost. Furthermore, the utilization of high-pressure CO_2 in synthesis requires an expensive pressure-resistant apparatus. Therefore, it is desirable to develop a reaction system that can

synthesize DRCs with low-pressure and low-concentration CO_2, which would lead to an ideal DRC synthesis by directly using exhaust gases from emission sources with a low-cost manufacturing apparatus.

In principle, DRC can be synthesized from CO_2 and alcohol by dehydration condensation, but the DRC yields are strictly limited by the reaction equilibrium, even under high-pressure CO_2 conditions, in which the initial side is much more stable in terms of the Gibbs free energy (Scheme 1a).[5] Therefore, dehydrating agents are generally used to remove coproduced water and shift the equilibrium toward DRC formation (Scheme 1b). Dehydrating agents that are recyclable or regenerable under mild reaction conditions are preferable, considering their environmental impact. The development of catalysts lowering the activation energy is one of the important
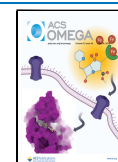
Scheme 1. Synthetic Routes to Dialkyl Carbonate from Alcohol and CO_2

a) Dehydration condensation

$$2\ ROH\ +\ CO_2\ \rightleftharpoons\ \underset{DRC}{RO\text{-}C(O)\text{-}OR}\ +\ H_2O\qquad \text{(Catalyst)}$$
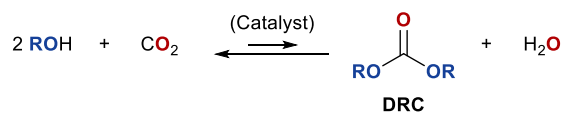
b) Dehydration condensation with dehydrating agent

$$2\ ROH\ +\ CO_2\ +\ DA\ (Dehydrating\ Agent)\ \rightleftharpoons\ RO\text{-}C(O)\text{-}OR\ +\ DA{\cdot}H_2O\qquad \text{(Catalyst)}$$

c) Alkylation

$$ROH\ +\ CO_2\ +\ RX\ \rightarrow\ RO\text{-}C(O)\text{-}OR\ +\ HX\qquad \text{(Catalyst)}$$
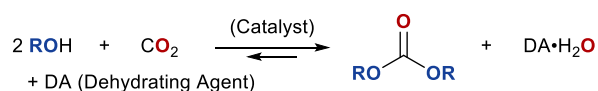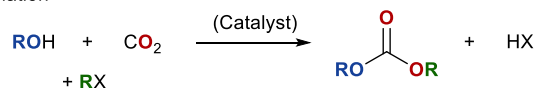
factors to effectively convert inert CO_2 into DRC.[6] Thus, the combination of catalysts and dehydrating agents has been explored and includes Ti(IV) compounds, Sn(IV) compounds, or CeO_2–ZrO_2 with acetal,[7−11] choline hydroxide/MgO or CeO_2 with epoxide,[12−14] CeO_2 with 2-cyanopyridine,[15] Cu-doped CeO_2 with methyl trichloroacetate,[16] CeO_2 with orthoester,[17] and CeO_2 with 2-furonitrile.[18] Imidazolium bicarbonate has been reported to function as both a dehydrating agent and a catalyst.[19,20] Despite the significant efforts devoted to this research area, achieving high yields of DRC using low-pressure CO_2 remains a challenging task. Tomishige et al. confirmed that the synthesis of DRC in excess acetonitrile as a dehydrating agent proceeds even at a low CO_2 pressure of 0.08 MPa, while the yield of DRC based on the alcohol used is limited.[21] Although DRC synthesis via alkylation of a monoalkyl carbonate ($[ROC(O)O]^-$) inter-mediate with alkyl halides might be an alternative approach to that of dehydration condensation (Scheme 1c),[4,22−24] the use of halogenated alkylating agents and disposal of wastes such as the coproduced halogen acids or neutralized salts are problematic from the viewpoint of green chemistry.

In reactions using low-pressure and low-concentration CO_2, the decrease in the reaction rate is a problem; however, more critical is the decrease in the amount of CO_2 in the reaction system, which is closely related to the aforementioned reaction equilibrium. The amount of CO_2 dissolved in organic solvents is usually low: the saturated solubility of CO_2 in MeOH and EtOH, which are both substrates and solvents for DRC synthesis, is reported to be 0.14 M (0.14 mmol CO_2 in 24.7 mmol MeOH) and 0.10 M (0.10 mmol CO_2 in 17.1 mmol EtOH), respectively, under atmospheric pressure.[25] Since the molar amount of CO_2 is much lower than that of alcohol substrates under the reaction conditions, the maximum achievable DRC yield based on the alcohol used must be low. Therefore, in this study, we focused on a chemical CO_2 capture reaction, the formation of monoalkyl carbonates ($[BASE\text{-}H][ROC(O)O]$) from CO_2, alcohols, and strong organic bases, to increase the amount of CO_2-equivalent species to the alcohol substrate in the reaction media without increasing the CO_2 pressure. Although monoalkyl carbonic acids ($ROC(O)OH$) are seldom formed from alcohols and atmospheric pressure of CO_2 under neutral conditions, $[BASE\text{-}H][ROC(O)O]$ are readily formed in the presence of organic strong bases such as 1,6-diazabicyclo[5,4,0]undec-7-ene

(DBU).[26] We have previously demonstrated that $[DBU\text{-}H][nBuOC(O)O]$ is generated in approximately 60% yield by simply bubbling 15 vol % CO_2 ($CO_2/N_2 = 15:85$, v/v) into a mixture of DBU (6.0 mmol) and nBuOH (6.5 mmol) in N-methyl-2-pyrrolidone under atmospheric pressure.[27] Because the formation of $[BASE\text{-}H][ROC(O)O]$ is reversible,[26] the chemical CO_2 capture reaction is expected to serve as an in situ molecular device to capture and release CO_2, thus ensuring a sufficient amount of CO_2 in the reaction media even with low-pressure and low-concentration CO_2. In addition, monoalkyl carbonates $[ROC(O)O]^-$ are often found as reaction intermediates in DRC synthesis; therefore, it is possible to construct reaction systems in which $[BASE\text{-}H][ROC(O)O]$ is directly involved in catalysis, depending on the catalyst used. Some research has been reported on application of CO_2 chemisorption such as the $[BASE\text{-}H][ROC(O)O]$ formation for synthesis of useful organic compounds.[28−36] In previous studies for diethyl carbonate (DEC) synthesis, Wu et al. and Kim et al. independently reported DRC synthesis in the presence of organic bases, but they do not address the formation of $[BASE\text{-}H][ROC(O)O]$ and its impact on the reaction outcome, nor did they investigated DRC synthesis under low-pressure and low-concentration CO_2.[19,37] By contrast, Liu et al. and Nozaki et al. accomplished DRC synthesis under low-pressure CO_2 via $[BASE\text{-}H][ROC(O)O]$; CH_2Br_2 and alkyl triflates were used as halogenated alkylating agents.[38,39] Herein, we report a cooperative combination of DBU for the chemical capture of CO_2, tetraalkyl orthosilicate ($Si(OR)_4$, TROS) as the dehydrating agent, and CeO_2 as the catalyst for the synthesis of DRC using atmospheric pressure CO_2 (Scheme 2). This system demonstrates environmentally

Scheme 2. Outline of This Work

✓ Low-pressure and low-concentration CO_2 available
✓ Absence of halogenated alkylating agents
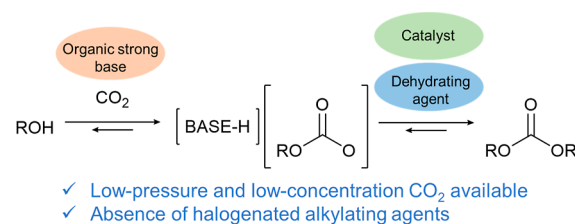
friendly DRC synthesis using low-pressure and low-concentration CO_2 without utilizing halogenated alkylating agents, even under reaction conditions with no large excess of either CO_2, alcohol, or a dehydrating agent.

■ RESULTS AND DISCUSSION

Evaluation of the Combination of the Catalyst and Dehydrating Agent. To apply the in situ chemical CO_2 capture reaction using DBU in DRC synthesis, negative interactions between DBU, dehydrating agents, and catalysts must be avoided, and particular attention should be paid to the strong basicity and nucleophilicity of DBU. In this context, we selected TROS as the dehydrating agent because we recently confirmed that TROS can act as an efficient dehydrating agent even in the presence of strong organic bases.[40] TROS reacts with coproduced water to form silanol, which is subsequently transformed into a thermodynamically stable disiloxane via a condensation reaction with another TROS. During the dehydration process, alcohols, the starting materials for DRC synthesis, are coproduced.[41] The ideal overall reaction is shown in Scheme 3, although the disiloxane can undergo

Scheme 3. Ideal Overall Reaction Equation for the DRC Synthesis Using TROS
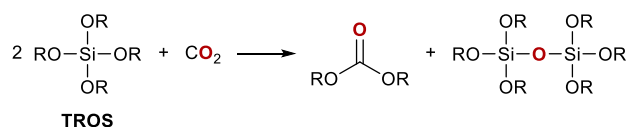
disproportionation or oligomerization upon further reactions with water or silanol. We used CeO_2 as a catalyst due to its established catalytic performance in DRC synthesis.[42] We hypothesized that CeO_2 pretreated under appropriate conditions would have few surface hydroxyl groups, thus avoiding undesired side reactions with TROS, and the moderate Lewis acidity of the active sites would prevent irreversible adsorption of organic strong bases.[43] Furthermore, it is noteworthy that, in the DRC synthesis catalyzed by CeO_2, the reaction rate was reported to be almost independent of the CO_2 pressure.[44]

Based on these findings, we synthesized DEC using a combination of DBU, tetraethyl orthosilicate (TEOS), and CeO_2 under atmospheric pressure CO_2. CeO_2 purchased from Sigma-Aldrich was pretreated by calcination at 600 °C in air,[15] where BET surface area was determined to be 40 m^2/g by N_2 adsorption/desorption analysis. The reaction was performed in a sealed reactor (volume: 11 mL). CeO_2 (172 mg) was added to a solution containing TEOS (16.0 mmol), DBU (8.0 mmol), and EtOH (8.0 mmol), followed by bubbling with 100 vol % CO_2 at a flow rate of 0.1 L/min for 10 min to generate [DBU-H][EtOC(O)O] in situ (Scheme 4). Subsequently, the

Scheme 4. Schematic Procedure for the DEC Synthesis with CO_2 bubbling. DA: Dehydrating Agent
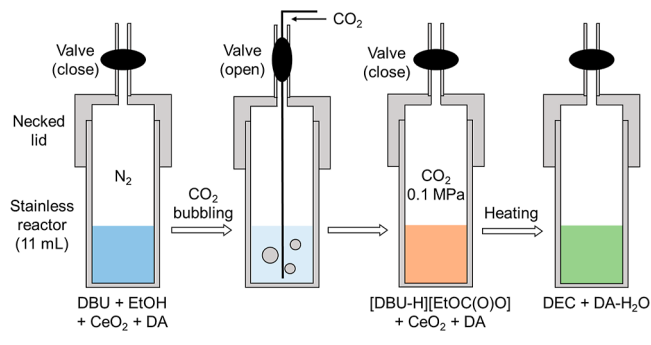
reactor was sealed and heated to 120 °C. Because the initial CO_2 pressure in the reactor before heating was atmospheric, the amount of CO_2 in the headspace of the reactor was approximately 5.8 mL (0.25 mmol). The amount of CO_2 captured as [DBU-H][EtOC(O)O] in the solution is estimated to be approximately 8.0 mmol, resulting in a total CO_2 amount of approximately 8.25 mmol in the reactor. Even under conditions in which neither excess CO_2, alcohols, nor dehydrating agents were present, we observed the formation of the desired DEC in significant yields (Figure 1); the amount of DEC produced steadily increased with reaction time, reaching a near plateau after 24 h, and finally, 3.11 mmol of DEC was obtained after 48 h. Because the theoretical amount of produced DEC was 8.0 mmol based on the initial amount of EtOH (8.0 mmol) and the amount of the in situ produced EtOH (8.0 mmol) by the reaction of TEOS with water, the DEC yield was calculated to be 39%. For comparison, 2-cyanopyridine (8.0 mmol), which has been reported as an
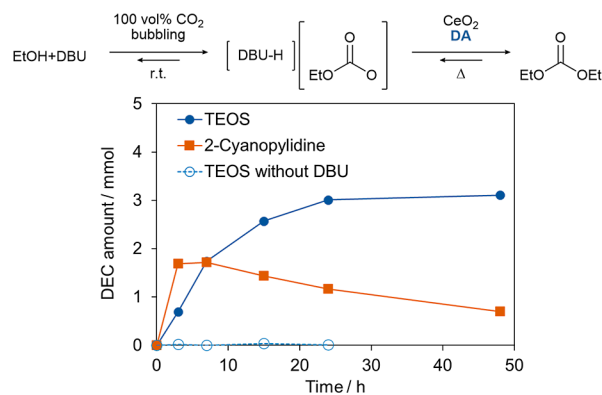

Figure 1. Time dependence of DEC yields using atmospheric pressure of CO_2. Reaction conditions: 8 mmol of EtOH, 172 mg of CeO_2, 16 mmol of TEOS or 8 mmol of 2-cyanopylidine, and 0.1 MPa of CO_2 (bubbling at 0.1 L/min for 10 min), with/without 8 mmol of DBU, heated at 120 °C. Blue closed circles and line: TEOS with DBU. Orange closed squares and line: 2-cyanopylidine with DBU. Blue open circles and line: TEOS without DBU.

efficient dehydrating agent in CeO_2-catalyzed DRC synthesis,[15] was used instead of TEOS. We observed a more rapid reaction in the initial stage, generating 1.69 mmol of DEC in 3 h; however, the DEC yield gradually decreased as the reaction time increased. As elucidated by Tomishige et al., 2-picolinamide, which is produced by dehydration with 2-cyanopyridine, can react with alcohol to yield alkyl picolinate and ammonia as byproducts, and the resulting ammonia further decomposes DEC into alkyl carbamate.[44] In our experiment, ethyl picolinate and ethyl carbamate were detected by GC−MS and ^1H NMR analysis, suggesting that the produced DEC decomposes in the presence of strongly basic DBU. Other homogeneous and heterogeneous catalysts were also evaluated under comparable reaction conditions; however, only CeO_2 exhibited significant catalytic activity (Tables S1 and S2). These results clearly indicate that the CeO_2/DBU/TEOS cooperative system, which combines CeO_2 as the catalyst and TEOS as the dehydrating agent in the chemical CO_2 capture reaction using DBU, is especially effective in overcoming the strict reaction equilibrium and synthesizing DEC in good yields without the use of high-pressure CO_2.

The CeO_2/DBU/$Si(OR)_4$ cooperative system can be applied to the synthesis of other DRC using the corresponding alcohols and TROS (Figure S2). Using nBuOH and tetrabutyl orthosilicate (TBOS), dibutyl carbonate (DBC) was obtained in 23% yield after 48 h. DBC formation proceeded almost constantly over 48 h but at a slower rate than that of DEC, probably because of the steric hindrance of the butyl group. Since tetramethyl orthosilicate (TMOS) and MeOH are highly volatile and are removed during CO_2 bubbling, in the synthesis of dimethyl carbonate (DMC), CO_2 was introduced by pressurization to 0.4 MPa without bubbling and CO_2 pressure was released to atmospheric pressure before heating. Under these conditions, the DMC yield was 2% after 24 h and 2% after 48 h. Although the details are unclear at this stage, because the disiloxane and the corresponding oligosiloxanes are involved in the reaction equilibrium, we hypothesize that their thermodynamic stability is responsible for the low yield.

Effect of CO_2 Pressure. We confirmed that DEC can be synthesized in good yields by simply bubbling CO_2 without pressurizing; however, to clarify the effect of the CO_2 pressure on the reaction efficiency, we performed a reaction in which

the CO_2 pressure was added after the CO_2 bubbling, and the results were compared with those obtained with the CO_2 bubbling only (Figure 2). The DEC yields were almost
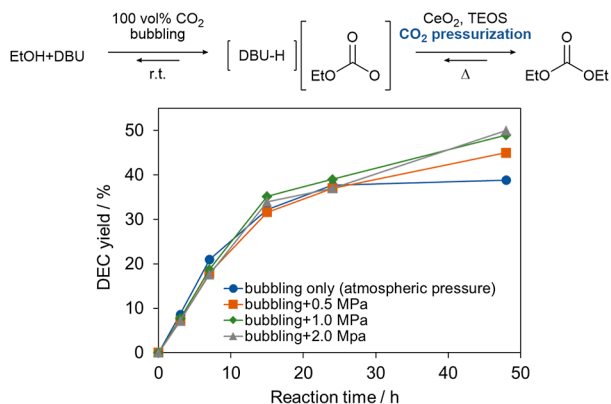

Figure 2. Dependence of DEC yield on the CO_2 pressure. Reaction conditions: 8.0 mmol of EtOH, 8.0 mmol of DBU, 172 mg of CeO_2, 16.0 mmol of TEOS, 0.1 MPa of CO_2 (bubbling at 0.1 L/min for 10 min), and heated at 120 °C. Blue circles and line: bubbling only. Orange squares and line: 0.5 MPa of CO_2 after bubbling. Green rhombs and line: 1.0 MPa of CO_2 after bubbling. Gray triangles and line: 2.0 MPa of CO_2 after bubbling.

identical up to 24 h, regardless of the CO_2 pressure, but the yields at 48 h were significantly different depending on the pressure: 39% (bubbling only), 45% (0.5 MPa of CO_2), 49% (1.0 MPa of CO_2), and 50% (2.0 MPa of CO_2). Extending the

reaction time to 72 h under pressurized conditions, the yields of DEC reached 42% (0.5 MPa), 51% (1.0 MPa), and 54% (2.0 MPa) (data points are not shown in Figure 2). As reported by Tomishige et al., the reaction rate of CeO_2-catalyzed DRC synthesis using 2-cyanopyridine as the dehydrating agent was almost constant and independent of the CO_2 pressure.[44] The reaction rate of our system using CeO_2 as a catalyst was similarly independent of the CO_2 pressure, although there was a difference when DBU and TEOS were used instead of 2-cyanopyridine. Therefore, the yields after 48 h depended on the CO_2 pressure, that is, the amount of CO_2 in the reactor, indicating that the influence of chemical equilibrium limited the DEC yields.

Effect of Organic Bases. As mentioned above, the formation of [BASE-H][ROC(O)O] is reversible, and [BASE-H][ROC(O)O] decomposes upon heating.[26] Thus, free DBU was present in the reaction medium from the initial stage of the reaction. Irreversible deactivation of CeO_2 by the adsorption of a free base onto Lewis acid sites is unlikely but may be reversibly inhibited. Therefore, we investigated the effect of organic bases to identify the optimal bases for DEC synthesis using CeO_2 and TEOS (Table 1), and the formation of [BASE-H][ROC(O)O] by CO_2 bubbling with each base was estimated, and the results are summarized in Table S3. When using a tertiary alkylamine, Hünig base, the yield of DEC was negligible (entry 1). Owing to its much lower basicity than that of DBU, almost no [BASE-H][ROC(O)O] was formed during CO_2 bubbling under atmospheric conditions. Tetramethylguanidine (TMG) exhibited strong basicity comparable to that of DBU, and sufficient [BASE-

Table 1. Influence of Organic Bases for DEC Synthesis under Atmospheric Pressure[a]

Entry	Base		pKa of conjugate acid in MeCN[45, 46]	Yield of DEC / %
1		Hünig base	18.8	< 1 (7 h)
2		TMG	23.3	1 (7 h)
3		DBN	23.89	8 (7 h) / 9 (48 h)
4		DBU	24.33	21 (7 h) / 39 (48 h)
5		MTBD	25.44	12 (7 h) / 30 (48 h)
6		TBD	25.98	7 (7 h) / 8 (48 h)

[a]Reaction conditions: 8.0 mmol of EtOH, 172 mg of CeO_2, 16.0 mmol of TEOS, and 0.1 MPa of CO_2 (bubbling at 0.1 L/min for 10 min), heated at 120 °C. [b]pKa values were from references 45 and 46.

H][ROC(O)O] were formed by the bubbling but afforded a DEC yield of only 1% (entry 2). We assumed that the N−H functional group had an adverse effect,[27] and ethyl *N,N*-dimethylcarbamate was detected by GC−MS analysis of the reaction mixture, indicating the decomposition of TMG. The reaction with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), which comprises an amidine scaffold similar to that of DBU and a comparable amount of [BASE-H][ROC(O)O] was formed by the bubbling, resulted in a yield of 8% at 7 h, with no significant improvement even upon extending the reaction time to 48 h (entry 3). The bicyclic guanidine analogues 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which have higher basicity than that of DBU, also afforded DEC (entries 5 and 6). While the DEC yield with MTBD was 12% at 7 h and increased to 32% at 48 h, the reaction with TBD, which has limited solubility in EtOH, led to a diminished yield. These results clearly show the significant impact of bases on DEC yields. Among the organic bases examined, DBU afforded the highest DEC yield. Although we have reported the synthesis of *N*-substituted carbamic acid esters from amines, TROS, and CO_2 using organic bases, such a large difference in the product yields was not observed when DBN, DBU, and MTBD were used as the bases.[40] Hence, we assume that the bases were adsorbed reversibly on CeO_2, and it is apparent that in addition to the basicity, other factors, such as steric hindrance around the basic nitrogen atoms, affected the yield. It is noteworthy that no significant byproducts were observed in the DEC synthesis with bases, except for TMG.

Although the number of Lewis acid sites on CeO_2 used in this study was not quantified, a large excess of bases (8.0 mmol) was present in the reaction media relative to the number of Lewis acid sites on CeO_2 (172 mg, 1.00 mmol). To further explore the effect of base adsorption onto the sites, we examined DEC synthesis under conditions in which the relative amount of DBU to the Lewis acid sites is reduced; i.e., we used a catalytic amount of DBU (0.5 mmol) (Figure 3). The reaction was performed under pressurized CO_2 conditions (0.5 MPa) because, with 0.5 mmol of DBU, CO_2 bubbling alone does not ensure enough CO_2 and [DBU-H][ROC(O)-O] in the reactor. For comparison, the reaction was also performed with 8.0 mmol of DBU under 0.5 MPa of CO_2. The reaction with 0.5 mmol DBU displayed a faster initial rate than
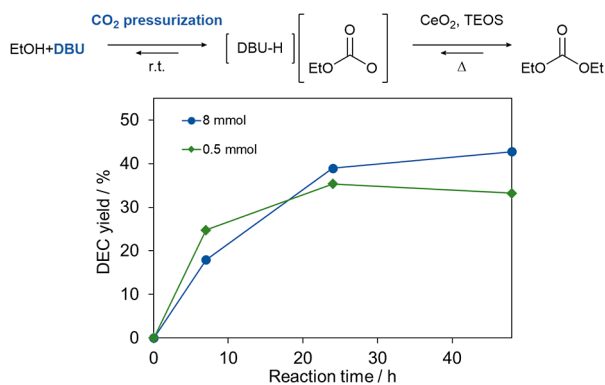

Figure 3. Dependence of DEC yield on the DBU amount. Reaction conditions: 8.0 mmol of EtOH, 8.0 or 0.5 mmol of DBU, 172 mg of CeO_2, 16.0 mmol of TEOS, and 0.5 MPa of CO_2 after bubbling at 0.1 L/min for 10 min, heated at 120 °C. Blue circles and line: 8.0 mmol of DBU. Green rhombs and line: 0.5 mmol of DBU.

that with 8 mmol DBU (18% at 7 h) and afforded a higher DEC yield of 25% at 7 h. By contrast, the reaction with 8 mmol of DBU afforded DEC in 43% yield at 48 h. The yield was higher than that obtained (33%) with 0.5 mmol of DBU because the captured CO_2 amounts in terms of [DBU-H][EtOC(O)O] were higher when higher amounts of DBU were used. Further experiments were performed with 0.5 mmol of other bases, namely, DBN and MTBD, under pressurized CO_2 conditions (0.5 MPa); DEC was obtained in 20 and 19% at 7 h and 29 and 28% at 48 h, respectively. Notably, the pronounced difference in DEC yields observed when using stoichiometric amounts of bases (Table 1) was no longer observed when catalytic amounts of bases were used. These results suggest that base adsorption on CeO_2 occurs reversibly rather than irreversibly, thus affecting the reaction rate but not the achievable yields. In addition, we individually determined that TEOS and the corresponding disiloxane did not adsorb onto and react with CeO_2.

Temperature Effect. The time dependence of DEC formation was measured at temperatures of 100, 120, and 140 °C (Figure 4). The reaction at 100 °C was slower, and an
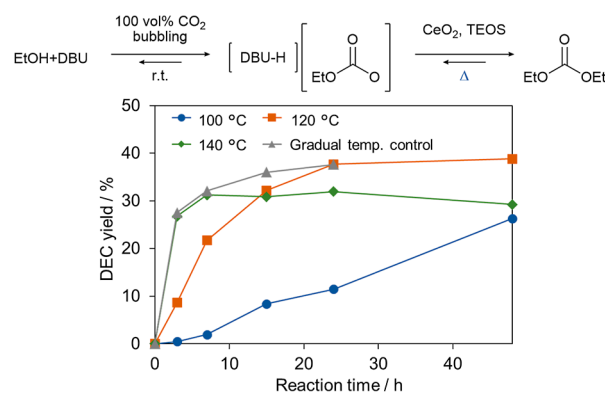

Figure 4. Dependence of DEC yield on reaction temperatures. Reaction conditions: 8.0 mmol of EtOH, 8.0 mmol of DBU, 172 mg of CeO_2, 16.0 mmol of TEOS, and 0.1 MPa of CO_2 (bubbling at 0.1 L/min for 10 min). Orange squares and line: 100 °C. Blue circles and line: 120 °C. Green rhombus and line: 140 °C. Gray triangles and line: 140 °C for 3 h to 120 °C for 10 h to 100 °C for 35 h.

almost linear increase in yield was observed after 48 h. Extending the reaction time to 72 and 96 h afforded 40 and 42% DEC, respectively (the data points are not shown in Figure 4). By contrast, at 140 °C, although the initial reaction rate increased notably, the maximum yield was lower than that at 120 °C. The DEC yields reached a plateau at all temperatures, suggesting that the reaction was governed by an equilibrium. This equilibrium shifts toward the DEC side as the reaction temperature decreases. In the synthesis of DMC by dehydration condensation from MeOH and CO_2, it is well known that a low reaction temperature favors the formation of DMC.[6] Although a simple comparison is difficult because the influence of the dehydrating agents cannot be ignored, the trend is consistent with that observed in our system.

By exploiting the features of this reaction system, namely, both the reaction rate was higher at higher temperatures, and the equilibrium yield was higher at lower temperatures; gradual temperature control was used to accomplish the maximum yield in a shorter reaction time (Figure 4; gray triangles and line). This reaction was performed at 140 °C for 3 h, after which the temperature was changed to 120 °C and held for 10

h (time profile of DEC yield with the temperature control is shown in Figure S3). Thereafter, the temperature was changed to 100 °C. While the DEC yield at 24 h was the same as that at 120 °C (38%), the yield at 15 h was higher than that of the reactions at 120 or 140 °C. This indicates that the temperature gradation method shows promise for our system.

Utilization of Low-Concentration CO_2. We next examined a reaction utilizing 15 vol % CO_2 (CO_2/N_2 = 15:85), a CO_2 concentration comparable to that of exhaust gas from coal-fired power plants, instead of 100 vol % CO_2 (Figure 5).[47,48] It was estimated from our previous report that bubbling
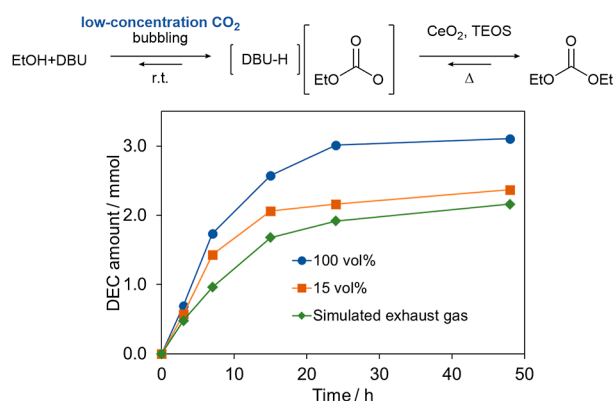

Figure 5. Dependence of DEC yield on gas types. Reaction conditions: 8.0 mmol of EtOH, 8.0 mmol of DBU, 172 mg of CeO_2, and 16.0 mmol of TEOS, heated at 120 °C. Blue circles and line: bubbling 100 vol % CO_2 at 0.1 L/min for 10 min. Orange squares and line: bubbling 15 vol % CO_2 (CO_2/N_2 = 15:85 v/v) at 0.1 L/min for 20 min. Green rhombs and line: bubbling simulated exhaust gas (CO_2: 15 vol %, SO_2: 500 ppm, NO_2: 500 ppm, CO: 300 ppm, and N_2: balanced) at 0.1 L/min for 20 min.

15 vol % CO_2 into a mixture of EtOH and DBU would produce $[DBU-H][EtOC(O)O]$ in approximately 60% yield.[27] Considering the CO_2 amount of ca. 0.038 mmol in the headspace, the total amount of CO_2 and its equivalent species in the reactor is approximately 4.8 mmol. Despite the lower amount of CO_2 compared with that in the reaction with 100 vol % CO_2 (the CO_2 amount is ca. 8.25 mmol), 2.37 mmol of DEC was obtained at 48 h (Figure 5, orange squares and line). The yield is ca. 30% based on EtOH and 49% based on CO_2. Furthermore, we confirmed that the reaction system could directly use simulated exhaust gas from coal-fired power plants containing CO_2 (15 vol %), SO_2 (500 ppm), NO_2 (500 ppm), and CO (300 ppm).[47,48] Although slightly diminished rates and yields were observed, 2.16 mmol of DEC was successfully generated (the yield was ca. 27% based on EtOH and ca. 45% based on CO_2). This result highlights that the reaction system combining the chemical CO_2 capture reaction using DBU with a CeO_2 catalyst and a TROS-based dehydrator shows promise to directly use exhaust gases for DRC synthesis, thereby avoiding energy- and cost-intensive steps such as separation, purification, and compression of emitted CO_2.

CONCLUSIONS

We have developed a novel approach to DRC synthesis using low-pressure and low-concentration CO_2 without using highly reactive, yet environmentally unfriendly, electrophiles such as alkyl halides. The approach involves three essential components. First, the formation of monoalkyl carbonate ($[BASE-$ $H][ROC(O)O]$) from an alcohol and a strong organic base increases the amount of CO_2 in the reaction system. Second, tetraalkyl orthosilicate served as a dehydrating agent, even in the presence of a strong organic base. Third, CeO_2 comprising minimal surface hydroxyl groups and moderate Lewis acid sites on its surface catalyzes DRC synthesis independent of CO_2 pressure. The $CeO_2/DBU/Si(OR)_4$ cooperative system was adaptable to various CO_2 sources, including 15 vol % CO_2, simulated exhaust gas of coal-fired power plants, and 100 vol % CO_2. These gases were used for DRC synthesis via bubbling to eliminate the need for pressurization. This system proceeds using nearly equal amounts of all components. Given the distinctive attributes of this reaction system, further enhancement of the reaction rate can be anticipated through the development of more optimal combinations of catalysts, bases, and dehydration agents. Thus, there is potential for future industrial applications of low-pressure and low-concentration CO_2-based DRC synthesis methods. Furthermore, the strategic cooperation of $[BASE-H][ROC(O)O]$ formation, dehydrating agents, and catalysts holds promise as a new methodology involving low-pressure and low-concentration CO_2 that may not be restricted to DRC synthesis but could be used for other CO_2 conversion reactions that require conventional high-pressure and high-purity CO_2. We anticipate that this approach will contribute to a broader landscape of sustainable CO_2 utilization and conversion.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c00284.

> General information; procedure of DRC synthesis; screening of catalysts; time dependence of DRC synthesis using TMOS and TBOS; yields of $[BASE-H][EtOC(O)O]$ using each base; and time profiles of DEC yield with gradual-temperature control (PDF)

AUTHOR INFORMATION

Corresponding Authors

Hiroki Koizumi − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;* ⓞ orcid.org/0000-0002-3518-5944; Email: h.koizumi@aist.go.jp

Jun-Chul Choi − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;* ⓞ orcid.org/0000-0002-7049-5032; Email: junchul.choi@aist.go.jp

Authors

Haruki Nagae − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan*

Katsuhiko Takeuchi − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;* ⓞ orcid.org/0000-0002-2720-5394

Kazuhiro Matsumoto − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;* ⓞ orcid.org/0000-0003-1580-8822

Norihisa Fukaya − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;* ⓞ orcid.org/0000-0001-8319-803X

Yoshiaki Inoue − *Tosoh Corporation, Yokkaichi, Mie 510-8540, Japan*

Satoshi Hamura − *Tosoh Corporation, Minato-ku, Tokyo 105-8623, Japan*

Takahiro Masuda − *Tosoh Corporation, Minato-ku, Tokyo 105-8623, Japan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c00284

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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