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## Introduction

Synthesis of useful compounds from carbon dioxide ( $CO_2$ ) is an important subject in synthetic organic chemistry.<sup>1,2</sup> Among various methods for  $CO_2$  fixation, the catalytic synthesis of cyclic carbonates from  $CO_2$  and epoxides has been extensively studied. Cyclic carbonates are used as monomers for polycarbonates, electrolytes for lithium-ion batteries, and polar aprotic solvents. Although some of them have been synthesized from 1,2-diols and phosgene on an industrial scale, this method has serious environmental loads caused by

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# Quaternary ammonium hydroxide as a metal-free and halogen-free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide<sup>†</sup>

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Tetrabutylammonium hydroxide (TBAH) and other quaternary ammonium hydroxides catalyzed the cycloaddition of  $CO_2$  to epoxides under solvent-free conditions to give cyclic carbonates. When TBAH was exposed to  $CO_2$ , TBAH was converted into tetrabutylammonium bicarbonate (TBABC), which was a catalytically active species. A D-labeled epoxide and an optically active epoxide were used to study the reaction mechanism, which invoked three plausible pathways. Among them, path A seemed to be predominant; the bicarbonate ion of TBABC attacks the less hindered C atom of the epoxide to generate a ring-opened alkoxide intermediate, which adds to  $CO_2$  to give a carbonate ion, and the subsequent cyclization yields a cyclic carbonate. Density functional theory (DFT) calculations successfully delineated the potential energy profile for each reaction pathway, among which path A was the lowest-energy pathway in accordance with the experimental results. The tetrabutylammonium (TBA) cation carries the positive charges on the H atoms, but not on the central N atom, and the positively charged H atoms close to the central N atom form an anion-binding site capable of stabilizing various anionic transition states and intermediates.

phosgene, which is highly toxic, and by the concomitant production of hydrogen chloride and waste solvent. This is why many catalysts for the production of cyclic carbonates from  $CO_2$  and epoxides have been developed, such as alkali metal salts,<sup>3</sup> metal complexes,<sup>4</sup> salen complexes,<sup>5</sup> ionic liquids,<sup>6</sup> organocatalysts,<sup>7</sup> quaternary ammonium salts,<sup>8</sup> and immobilized catalysts.<sup>9</sup> Some of them, however, have problems, such as the use of organic solvent and co-catalysts, the formation of by-products, and the corrosion of reactor vessels.

We have developed quaternary phosphonium salts immobilized on mesoporous silica,<sup>10</sup> quaternary ammonium betaine organocatalysts,<sup>11</sup> and metalloporphyrins bearing quaternary ammonium bromide groups.<sup>12</sup> In screening various quaternary onium salts, we found that tetrabutylammonium hydroxide (TBAH) showed much higher catalytic activity and selectivity than expected. Because catalysts for this particular reaction need a good leaving ability as well as high nucleophilicity, TBAH is considered to be unsuitable because of the poor leaving ability of the hydroxide ion (OH<sup>-</sup>). TBAH has been used as a co-catalyst together with Co salen-type catalysts,<sup>5a</sup> and DABCO-type quaternary ammonium hydroxides have been employed as a catalyst.13 However, no detailed studies have been reported. In view of the metal-free, halogen-free, and solvent-free reaction promoted by a simple and inexpensive reagent such as TBAH, we decided to investigate the

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. Atomic coordinates of the optimized structures along path A. Comparison between  $\alpha$  and  $\beta$  attacks in the initial ring-opening step. Optimized structures along paths B and C. See DOI: 10.1039/c5cy00020c

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catalytic behavior of TBAH in detail. In particular, a halogenfree system is required because the use of halogen sometimes colors a product and corrodes a reactor made of metal. Herein we report the reaction mechanism of the TBAH-catalyzed synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>.

### Results and discussion

We examined various quaternary ammonium hydroxides. A commercially available solution of quaternary ammonium hydroxide in MeOH was evaporated to dryness to afford a powder in most cases, which was used as a catalyst. A 30 mL stainless autoclave was charged with 1,2-epoxyhexane (1a) (10.0 mmol), a catalyst, and  $CO_2$  (initial pressure, 1 MPa), and the mixture was heated at a constant temperature for 24 h. The results are summarized in Table 1. Cyclic carbonate 2a was obtained with TBAH in 94% yield (entry 1). In sharp contrast, Me<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>, which is less bulky than TBAH, gave 2a in only 2% yield (entry 2). This is probably due to the poor solubility of  $Me_4N^+OH^-$  in epoxide 1a. When choline hydroxide (HOCH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>Me<sub>3</sub>OH<sup>-</sup>) and BnN<sup>+</sup>Me<sub>3</sub>OH<sup>-</sup> were used, the yields increased up to 55% and 96%, respectively (entries 3 and 4). In general, the bulkier the quaternary ammonium cation, the higher the nucleophilicity of the counter anion.<sup>14</sup> However, the hexyl group, which is bulkier than the butyl group, decreased the catalytic activity (entry 5). The reaction with tetrabutylphosphonium hydroxide gave 2a in 22% yield (entry 6). When KOH and NaOH were used, no

Table 1 Screening of catalysts and optimization of the reaction conditions  $a^{a}$ 

|                | Bu + CO <sub>2</sub><br>Bu (1 MPa)<br><b>1a</b>                                  | catalyst<br>24 h   | Bu 2a         |                           |
|----------------|--|--------------------|---------------|---------------------------|
| Entry          | Catalyst   | Catalyst<br>(mol%) | Temp.<br>(°C) | Yield <sup>b</sup><br>(%) |
| 1              | $Bu_4N^+OH^-$ (TBAH)   | 3                  | 120           | 94                        |
| 2              | Me <sub>4</sub> N <sup>+</sup> OH <sup>-</sup>                                   | 3                  | 120           | 2                         |
| 3              | HOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> Me <sub>3</sub> OH <sup>-</sup> | 3                  | 120           | 55                        |
| 4              | BnN <sup>+</sup> Me <sub>3</sub> OH <sup>-</sup>                                 | 3                  | 120           | 96                        |
| 5 <sup>c</sup> | $Hex_4N^+OH^-$   | 3                  | 120           | $41^d$                    |
| 6              | $Bu_4P^+OH^-$  | 3                  | 120           | 22                        |
| 7              | NaOH   | 3                  | 120           | 0                         |
| 8              | КОН  | 3                  | 120           | 0                         |
| 9              | Bu <sub>3</sub> N  | 3                  | 120           | 13                        |
| 10             | TBAH   | 0.5                | 120           | 76                        |
| 11             | $Bu_4N^+Br^-$ (TBAB)   | 0.5                | 120           | 84                        |
| 12             | TBAH   | 1                  | 120           | 100                       |
| 13             | TBAH   | 1                  | 140           | 86                        |
| 14             | TBAH   | 1                  | 100           | 85                        |
| 15             | TBAH   | 1                  | 80            | 45                        |
| 16             | TBAH   | 1                  | 60            | 22                        |

<sup>*a*</sup> Conditions: epoxide 1a (10.0 mmol), catalyst (amount indicated above), CO<sub>2</sub> (1 MPa) in a 30 mL stainless autoclave. <sup>*b*</sup> Determined by <sup>1</sup>H NMR using 2-methoxynaphthalene as an internal standard. <sup>*c*</sup> 10% in MeOH. <sup>*d*</sup> Dimethyl carbonate (7%) as a by-product.

products were obtained (entries 7 and 8). These results indicate that the quaternary ammonium cation plays a vital role in catalysis as revealed recently.<sup>12c</sup> Tributylamine, which may be generated by the Hofmann degradation of TBAH, gave 2**a** in 13% (entry 9). Even when the catalyst loading of TBAH was decreased to 0.5 mol%, 2**a** was obtained in 76% yield (entry 10), which was slightly lower than the yield (84%) obtained with tetrabutylammonium bromide (TBAB) (entry 11).

We next optimized the reaction conditions. The best amount of TBAH was 1 mol%, and 2a was obtained in 100% yield (entry 12). When temperature was changed from 60 to 140 °C in the presence of 1 mol% TBAH, the highest yield was achieved at 120 °C (entries 12-16). Fig. 1 shows the time course of the reaction under the optimized conditions (catalyst loading, 1 mol%; CO<sub>2</sub> pressure, 1 MPa; and 120 °C). The reaction proceeded smoothly for 3 h, and the yield increased gradually over 24 h. The substrate scope of the TBAH-catalyzed reaction was investigated under the optimized conditions (Table 2). Various epoxides were selectively and cleanly converted into the corresponding cyclic carbonates in moderate to high yields, and no by-products such as 1,2-diol were detected. The products with the electronwithdrawing groups were obtained in good to excellent yields (entries 3, 5, 9, and 10). Cyclohexene oxide (1f) reacted with  $CO_2$  to afford 2f in high yield (entry 6), whereas epoxide 1g with a five-membered ring was converted into 2g in modest yield (entry 7). The substrate bearing the t-Bu group gave the product in moderate yield (entry 8).

Scheme 1 shows two representative mechanisms. In path 1, a nucleophile (Nu<sup>-</sup>) attacks the epoxide to produce an alkoxide ion, which adds to CO<sub>2</sub> to give a carbonate ion. The subsequent cyclization yields the product. In path 2, on the other hand, a carbonate ion is first produced, which then attacks the epoxide to generate an alkoxide ion. The fivemembered ring formation gives a cyclic carbonate. The trans and cis cyclic carbonates are obtained via paths 1 and 2, respectively, starting from the trans epoxide (Scheme 1). Soft nucleophiles often promote the reactions via path 1,12 while hard nucleophiles, such as N-heterocyclic carbenes and quaternary ammonium betaines,96,11 promote the reactions via path 2. On the other hand, TBAH is not simple because hydroxide has good nucleophilicity and yet a poor leaving ability, and the TBAH-catalyzed reaction may proceed via path 2 because hydroxide is a hard anion.

To clarify the reaction mechanism, we used deuterated *trans* epoxide 1k (Scheme 2).<sup>15</sup> The reaction *via* path 1 would give *trans*-2k, while that *via* path 2 would afford *cis*-2k. When the reaction was carried out under the optimized conditions, *trans*-2k and *cis*-2k were obtained in a ratio of 89:11. This result suggests that the reaction proceeds mainly *via* path 1 contrary to our expectation. However, as mentioned above, it is inappropriate to conclude that the reaction proceeds *via* path 1 because  $OH^-$  is a poor leaving group. It is more reasonable to assume the *in situ* formation of tetrabutyl-ammonium bicarbonate (TBABC) (Scheme 3) because the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) is a good nucleophile with a high



Fig. 1 Time course of the formation of 2a from 1a (10.0 mmol) and CO<sub>2</sub> (1 MPa) with TBAH (1 mol%) at 120  $^\circ\text{C}$  in a 30 mL stainless autoclave.

leaving ability. In the literature, TBABC was generated by bubbling CO2 gas into a solution of TBAH in MeOH for 10 min.<sup>16</sup> The catalytic activity of TBABC was unknown, although tetrabutylammonium methylcarbonate was used as a co-catalyst in the Co(salen)-catalyzed reaction of the epoxide with CO<sub>2</sub>.<sup>17</sup> We therefore prepared TBABC [IR (KBr): 1653 cm<sup>-1</sup>; <sup>13</sup>C NMR (*d*<sub>6</sub>-DMSO): 155 ppm; MS (FAB, negative): 61 for  $HCO_3^{-1}$  according to the literature method<sup>16</sup> and used TBABC as a catalyst instead of TBAH under the reaction conditions shown in Table 1 (entry 1), obtaining 2a in 89%. DFT calculations indicated that the formation of TBABC (Scheme 3) is very exothermic (-49.0 kcal mol<sup>-1</sup>) with no activation barrier. These results strongly suggest that TBABC generated in situ is a catalytically active species, which prompted us to explore other pathways similar to path 1, assuming the formation of TBABC. We further investigated the mechanism of the TBAH-catalyzed reaction from the viewpoint of stereochemistry using (R)-1d (Scheme 4). Although (R)-1d has

|       | 2                          | 2                                  |                              |                                     |
|-------|----------------------------|------------------------------------|------------------------------|-------------------------------------|
| R1    | 0<br>R <sup>2</sup> +<br>1 | CO <sub>2</sub> —<br>(1 MPa)       | BAH (1 mol%)<br>120 °C, 24 h | $R^1$ $R^2$                         |
| Entry | 1                          | $\mathbb{R}^1$                     | $R^2$                        | Yield <sup><math>b</math></sup> (%) |
| 1     | 1a                         | Bu                                 | Н                            | 89                                  |
| 2     | 1b                         | Me                                 | Н                            | 66                                  |
| 3     | 1c                         | CH <sub>2</sub> OMe                | Н                            | 90                                  |
| 4     | 1d                         | Ph                                 | Н                            | 88                                  |
| 5     | 1e                         | $CH_2Cl$                           | Н                            | 74                                  |
| 6     | 1f                         | $-(CH_2)_4-$                       |                              | 65                                  |
| 7     | 1g                         | -(CH <sub>2</sub> ) <sub>3</sub> - |                              | 42                                  |
| 8     | 1h                         | <i>t</i> -Bu                       | Н                            | 53                                  |
| 9     | 1i                         | CH <sub>2</sub> O <i>i</i> -Pr     | Н                            | 68                                  |
| 10    | 1j                         | CH <sub>2</sub> OPh                | Н                            | 94                                  |

 Table 2
 Synthesis of various cyclic carbonates with TBAH<sup>a</sup>

 $^a$  Conditions: epoxide (10.0 mmol), TBAH (1 mol%), CO $_2$  (1 MPa) in a 30 mL stainless autoclave.  $^b$  Isolated yield.



Scheme 1 Two typical reaction mechanisms for the synthesis of cyclic carbonates from epoxides and  $\mbox{CO}_2.$ 

previously been converted selectively into (*R*)-2d in the literature,<sup>12*a*,18</sup> TBAH gave (*R*)-2d and (*S*)-2d in a ratio of 87:13. This result indicates that the reaction was partially accompanied by the inversion of configuration to give (*S*)-2d, which is inaccessible from both path 1 and path 2.

Based on the above results (Schemes 2 and 4 and DFT calculations), we considered four reaction pathways shown in Scheme 5, where the reactions are represented by using a deuterated (2R)-*trans* epoxide to clearly distinguish each reaction pathway. Path A involves the double inversion processes as follows: a bicarbonate ion attacks the less hindered C atom of the epoxide to produce an alkoxide intermediate, which adds to CO<sub>2</sub> to give a carbonate ion. The subsequent cyclization affords a (4R)-*trans* cyclic carbonate. Path B branches from path A; the intramolecular proton transfer followed by cyclization gives a configurationally inverted product, a (4S)-*trans* cyclic carbonate. Because only path B



Scheme 2 Investigation of the reaction mechanism by using a D-labeled epoxide.



Scheme 3 In situ formation of TBABC from TBAH and CO2.

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Scheme 4 Investigation of the reaction mechanism by using an optically pure epoxide.



Scheme 5 Possible reaction pathways for the TBABC-catalyzed formation of cyclic carbonates from epoxides and  $CO_{2^r}$  where a deuterated (2*R*)-*trans* epoxide is used to clearly distinguish each reaction pathway.

gives the (4*S*)-product (Scheme 5), (*S*)-2d in Scheme 4 was produced probably *via* path B. Path C also branches from path A; the intramolecular attack of the alkoxide O atom on the carbonyl C atom affords a (4*R*)-*cis* cyclic carbonate. Because only path C gives the *cis* product (Scheme 5), *cis*-2k in Scheme 2 may have been formed *via* path C. Path D, which is initiated by the  $\alpha$  attack, was ruled out by density functional theory (DFT) calculations (Fig. S1, ESI<sup>†</sup>).<sup>19</sup> Because it is only path A that gives the (4*R*)-*trans* product, it is most likely that path A is predominant.

We performed DFT calculations to gain a deeper insight into the reaction mechanism.<sup>6g,7c,8e,20</sup> The potential energy

profiles for the TBABC-catalyzed reactions of propylene oxide (1b) with  $CO_2$  are shown in Fig. 2, and the optimized structures are given in Fig. 3. Fig. 4 represents the electrostatic properties of the tetrabutylammonium (TBA) cation and tributylamine for comparison. The TBA cation carries the positive charges on the H atoms, but not on the central N atom (Fig. 4a), and the positively charged H atoms close to the central N atom form a flexible anion-binding site, which is well represented by the large positive area of the isoelectrostatic potential surface (Fig. 4b).<sup>12c</sup> In contrast, the neutral counterpart, tributylamine, has no such positive regions (Fig. 4b). The initial ring-opening reaction  $(R \rightarrow TS_1 \rightarrow I_1)$ , which is common to all the paths, takes place with an activation energy of 25.9 kcal mol<sup>-1</sup>, and this is the rate-determining step because of the highest energy level.<sup>12c</sup> The resulting intermediate I\_1 is 15.8 kcal mol<sup>-1</sup> higher in energy than reactant R. The optimized structures with atomic charges for R, TS\_1, and I\_1 are shown in Fig. 3a-c. The negative charges in R are located in the bicarbonate moiety, and one of the negatively charged O atoms occupies the anion-binding site of the TBA cation. A small portion of the negative charge in R migrates to the epoxide in TS\_1, and the charge of the leaving O atom becomes -0.95 in I\_1. As seen in Fig. 3c, this negatively charged O atom is out of the anion-binding site. Therefore, I\_1 changes into more stable intermediate I\_1', where the negatively charged O atom is located at the anion-binding site. This relaxation results in a stabilization of 10 kcal mol<sup>-1</sup> (Fig. 3d), which clearly indicates the significant contribution of the TBA cation to the stabilization of the anionic species.<sup>12c</sup>

In path A, the ring-opened intermediate I\_1' accepts CO<sub>2</sub> at the negatively charged O atom to generate intermediate  $I_2$ , which is about 30 kcal mol<sup>-1</sup> lower in energy than  $I_1'$ . This substantial stabilization originates from the C-O bond formation and the delocalization of the negative charge over the carbonate moiety (the resonance effect). Although TS\_2 was found at -4.3 kcal mol<sup>-1</sup> (Fig. 3e), a precursor complex prior to TS\_2 could not be found probably because of the very small activation energy for TS\_2. The negative charges in intermediate I\_2 shift to the leaving bicarbonate moiety in TS\_3 (Fig. 3f and g), and the ring is closed with an activation energy of 20.2 kcal mol<sup>-1</sup> to afford product P. The relative potential energy of P is -36.9 kcal mol<sup>-1</sup>. The negatively charged bicarbonate ion in P is located at the anionbinding site of the TBA moiety, and the cyclic carbonate produced is also stabilized by the TBA moiety (Fig. 3h).

Path B is derived from intermediate  $I_2$  (Fig. 2). Each structure in path B is given in Fig. S2 (ESI<sup>†</sup>). The C–O bond rotation in the OCO<sub>2</sub>H moiety of  $I_2'$  leads to intermediate  $I_3b$  via TS\_3b, and the proton of the OCO<sub>2</sub>H moiety of  $I_3b$  is transferred to the OCO<sub>2</sub><sup>-</sup> moiety to give intermediate  $I_4b$  via TS\_4b. This proton transfer occurs with a very small activation barrier (1.5 kcal mol<sup>-1</sup>). Subsequently, the ring-closing reaction takes place with an activation energy of 35.1 kcal mol<sup>-1</sup>, which is much larger than that of path A (20.2 kcal mol<sup>-1</sup>). This unfavorable ring-closure in path B

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Fig. 2 Potential energy profiles for the TBABC-catalyzed reactions of propylene oxide (1b) with CO<sub>2</sub>. Computations were performed at the  $\omega$ B97XD/6-31G\* level with the self-consistent reaction field (SCRF) method (Et<sub>2</sub>O). The relative potential energies based on reactant R are shown in parenthesis in kilocalories per mole. The energy of an isolated CO<sub>2</sub> is included in the epoxide ring-opening step even if CO<sub>2</sub> does not appear explicitly. Paths A, B, C, and C' are shown in red, blue, black, and purple, respectively. The TBA cation is omitted from the structures.



Fig. 3 Optimized structures of (a) reactant R, (b) transition state TS\_1, (c) intermediates I\_1, (d) I\_1', (e) TS\_2, (f) I\_2, and (g) TS\_3, and (h) product P in the TBABC-catalyzed reaction of propylene oxide (1b) with  $CO_2$  (path A).

results from the nucleophilic attack at the sterically hindered secondary C atom. In addition, the leaving bicarbonate group stays a little far from the TBA cation in path B. The positions

of the leaving bicarbonate in both cases (paths A and B) are compared in Fig. S3 (ESI $\dagger$ ). The bicarbonate ion in path B is outside the electrostatic isosurface of +0.1 au, while that in



**Fig. 4** Electrostatic properties of the TBA cation (left) and tributylamine (right) calculated at the  $\omega$ B97XD/6-31G\* level. (a) The natural atomic charges. The charges at the equivalent atoms are averaged. (b) The isoelectrostatic potential represented by two orthogonal slices. The units are given in atomic unit. At the +0.10 au, a -1 point-charge gains a coulombic stabilization of 63 kcal mol<sup>-1</sup>. Three of the four anion-binding sites in the TBA cation are shown in pink circles.

path A is partially inside the surface of +0.1 au. The bicarbonate ion in **P\_b** shifts to a more stable position to yield product **P**.

Path C is derived from intermediate I\_1' (Fig. 2). Each structure in path C is given in Fig. S4 (ESI<sup>+</sup>). The C-C bond is rotated with an activation energy of 4.0 kcal  $mol^{-1}$  (TS\_2c). The negatively charged O atom in I\_2c attacks the carbonyl C atom of the OCO<sub>2</sub>H moiety to form a five-membered ring (I\_3c). This ring-closing reaction occurs with a very small activation energy  $(1.5 \text{ kcal mol}^{-1} \text{ for TS}_3c)$ . On the other hand, there is a larger barrier (15.4 kcal mol<sup>-1</sup>) for **I\_3c** to release OH<sup>-</sup>. This is because the C–O  $\sigma$ -bond is broken, which can be partially compensated by a C–O  $\pi$ -bond formation, and because the poor leaving group, OH<sup>-</sup>, with a localized negative charge is released. The OH<sup>-</sup> ion, which stays at the anion-binding site of TBA in intermediate I\_4c, then reacts with an extra CO2 molecule to form the bicarbonate ion and product P\_c. The bicarbonate ion in P\_c shifts to a more stable position to give product P. Interestingly, we found a much lower-energy process (path C'), where the leaving  $OH^-$  group in I\_3c', a complex of I\_3c with  $CO_2$ , is directly transferred to CO<sub>2</sub> to give off a bicarbonate ion (Fig. 2). This step requires a much smaller activation energy  $(7.7 \text{ kcal mol}^{-1}).$ 

Fig. 2 indicates that the reaction mechanisms are not straightforward. However, because all the reaction pathways (paths A-C') have a common intermediate,  $I_1'$ , the

succeeding pathways determine the selectivity of the whole reaction (product distribution). Paths A and B are more favorable than paths C and C' because in the former cases,  $I_1I'$  falls into an energy trough in the presence of CO<sub>2</sub>. Path A is the most favorable because path A has a much smaller activation energy (20.2 kcal mol<sup>-1</sup>) than path B (35.1 kcal mol<sup>-1</sup>). The reaction can also proceed *via* path C' as a minor pathway. These predictions are consistent with the experimental results shown in Schemes 2 and 4. Although the reaction rates may depend not only on the energy levels of the transition states but also on the diffusion efficiency of CO<sub>2</sub>, the observed selectivity can be well explained based on the former in this case.

### Conclusions

Carbon dioxide (CO<sub>2</sub>) is expected to be an important renewable feedstock for various useful organic compounds. The synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> under solvent-free conditions is one of the most atom-efficient CO<sub>2</sub> fixation methods. Here we have demonstrated that TBAH is a metal-free and halogen-free organocatalyst suitable for this reaction. The halogen-free system may find practical applications because the use of halogen sometimes colors a product and corrodes a reactor made of metal. Upon exposure to CO<sub>2</sub>, TBAH is converted into tetrabutylammonium bicarbonate (TBABC), which is a catalytically active species. Two experiments using a D-labeled epoxide and an optically active epoxide revealed that three paths, A-C, proceeded competitively, among which path A was likely to be the most favorable. Density functional theory (DFT) calculations successfully delineated the potential energy profile for each reaction pathway. The tetrabutylammonium (TBA) cation carries the positive charges on the H atoms, but not on the central N atom, and the positively charged H atoms close to the central N atom form an anion-binding site that can stabilize various anionic transition states and intermediates. The lowest-energy process was confirmed to be path A in accordance with the experimental results. The ratedetermining step was the initial ring-opening reaction of the epoxide by TBABC, and the subsequent CO<sub>2</sub> addition and cyclization gave a cyclic carbonate with the regeneration of TBABC.

### **Experimental section**

#### Synthesis of 4-deuterio-5-octyl-1,3-dioxolan-2-one

A 30 mL stainless autoclave was charged with trans-1deuterio-1,2-epoxydecane (1k) (1.58 g, 10.0 mmol),<sup>15</sup> TBAH (26.7 mg, 1 mol%), and then CO<sub>2</sub> (initial pressure, 1 MPa at room temperature). The mixture was heated with stirring at 120 °C for 24 h. The reactor was cooled in an ice bath for 20 min, and excess CO2 was released carefully. The crude product was dissolved in Et<sub>2</sub>O. The NMR yield was determined by using 2-methoxynaphthalene as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc (7:1)) gave a mixture of trans- and cis-4deuterio-5-octyl-1,3-dioxolan-2-one (87%, trans: cis = 89:11) as a colorless oil. trans-4-Deuterio-5-octyl-1,3-dioxolan-2-one. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  0.88 (t, J = 6.7 Hz, 3H), 1.27–1.48 (m, 12H), 1.62-1.72 (m, 1H), 1.75-1.85 (m, 1H), 4.05 (d, J = 7.2 Hz, 1H), 4.70 (q, J = 6.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.1, 22.6, 24.4, 29.10, 29.13, 29.3, 31.8, 33.9, 69.2 (t, J = 23.4 Hz), 77.1, 155.2; IR (neat) 2928, 2857, 1802, 1466, 1368, 1169, 1065, 773, 714 cm<sup>-1</sup>; HRMS (EI) calcd. for C<sub>11</sub>H<sub>19</sub>DO<sub>3</sub>: 201.1475, found 201.1460 ([M<sup>+</sup>]). cis-4-Deuterio-5octyl-1,3-dioxolan-2-one. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  0.88 (t, J = 6.7 Hz, 3H), 1.27-1.48 (m, 12H), 1.62-1.72 (m, 1H),1.75–1.85 (m, 1H), 4.51 (d, J = 7.4 Hz, 1H), 4.70 (q, J = 6.7 Hz, 1H);  ${}^{13}$ C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  14.1, 22.6, 24.4, 29.10, 29.13, 29.3, 31.8, 33.9, 69.1 (t, *J* = 23.2 Hz), 77.1, 155.2.

#### **Computational details**

All the computations were done with Gaussian 09.<sup>21</sup> Density functional theory (DFT) calculations at the  $\omega$ B97XD<sup>22</sup>/6-31G\* level were carried out to obtain the optimized structures and the potential energies. The solvation effect was included with the self-consistent reaction field (SCRF) method, and the dielectric constant of Et<sub>2</sub>O was used.<sup>23</sup> Natural population analysis (NPA) was performed with NBO ver 3.1 in the Gaussian package.<sup>24</sup> The transition-state structures were verified by frequency calculations.

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