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Efficient and Practical Organocatalytic System for Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides: 3-Hydroxypyridine/TBAI

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An efficient and practical organocatalytic system comprising 3-hydroxypyridine and tetra-*n*-butylammonium iodide was developed for the synthesis of cyclic carbonates from carbon dioxide and epoxides under mild conditions (1 atm CO₂, 25–60 °C) without organic solvent. By comparing with related hydroxypyridine derivatives, the effects of the hydroxyl group, the acidity and the steric factor, were discussed. Study on the mixtures of CO₂ and N₂ in various ratios indicated that the yield depends on CO₂ content, due to the solubility of CO₂ in the reaction mixture. The system was also shown not to be deteorated by the presence of H₂O, air or O₂.



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1. Introduction

Current CO_2 emissions into the earth's atmosphere have raised serious environmental and societal concerns in connection with the effect of CO_2 on global warming as a major greenhouse gas. As the main sources of CO_2 emission are the combustion of carbonaceous materials and animal metabolism, the reduction of CO_2 production has become an important and challenging research topic.^{1,2} As an abundant, nontoxic, nonflammable, easily available, and renewable carbon resource, CO_2 is a very attractive carbon feedstock.³⁻⁸ Therefore, the chemical fixation of CO_2 into valuable organic chemicals has attracted much attention as a goal of environmental protection and sustainable development. One of the most successful examples is the synthesis of cyclic carbonates from CO_2 and epoxides. These carbonates are valuable chemicals that can be used as polar aprotic solvents, electrolytes for lithium secondary batteries, and synthetic intermediates for pharmaceuticals and polymers.⁹⁻¹³

In past decades, various homogeneous and heterogeneous catalysts have been developed for coupling reactions between CO_2 and epoxides, including metal oxides,^{14,15} modified molecular sieves,^{16,17} alkali metal salts,¹⁸ organometallic complexes,^{19,20} and ionic liquids.²¹⁻²⁶ However, many of these catalytic systems require high temperatures, high CO_2 pressures, or toxic polar solvents and the reaction under milder conditions is still an active research topic.

Many metal-based catalytic systems have been developed for the synthesis of cyclic carbonates. In recent years, on the other hand, the number of organocatalytic systems has been drastically increasing because organocatalysts offer several advantages, being inexpensive, robust, nontoxic, and bench-stable.²⁷ Until now, several organocatalysts that contain functionality such as hydroxy groups,²⁸⁻³³ amino groups,³⁴ and carboxy groups³⁵ have been well recognized for playing important roles frequently combined with a halide salt as a co-catalyst. Such organocatalysts activate an epoxide and/or CO₂ to

facilitate the nucleophilic ring-opening of the epoxide by the halide ion and/or following addition reaction with CO_2 . Recently, we developed an organocatalytic system composed of 2-hydroxymethylpyridine and tetra-*n*-butylammonium iodide (TBAI).³⁶ We proposed that 2-hydroxymethylpyridine serves as a bifunctional catalyst and its hydroxyl group (hydrogen-bonding donor) and nitrogen atom (Lewis base) activate the epoxide and coordinate to CO_2 , respectively.^{37,38} As a new organocatalyst with a stronger hydrogen-bonding donor group, herein, we report 3-hydroxypyridine/TBAI as a new catalyst system for the synthesis of cyclic carbonates under mild and economical conditions such as solvent-free, atmospheric pressure of CO_2 , moderate temperature (Scheme 1).



Scheme 1. Synthesis of cyclic carbonates from CO₂ and epoxides.

2. Results and discussion

2.1. Reaction with hydroxypyridine-TBAI systems

Although the application of various organic bases to CO_2 activation or absorption has been reported,³⁹⁻⁴⁴ we have shown that pyridine is not a good catalyst for the cycloaddition of CO_2 and epoxides in the presence of TBAI at ambient pressure.³⁶ However, as mentioned above, hydroxy groups are good activators of epoxides due to hydrogen bond formation.^{28-33,36} Therefore, hydroxypyridines were expected to be alternative catalysts for the cycloaddition of CO_2 and epoxides. We studied three hydroxypyridine isomers **1–3** (Scheme 2) as simple and easily available organocatalysts, in combination with tetra-*n*-butylammonium halide as a co-catalyst, to form a new catalytic system for the synthesis of cyclic carbonate from CO_2 and epoxides.



Scheme 2. Structures of hydroxypyridines and pKa values of the hydroxy groups.

Catalysts 1–3 were screened with the same amount of TBAI as a co-catalyst using 1,2-epoxyhexane (4a) as a substrate at 40 °C under atmospheric pressure of CO₂ for 24 h. The results are summarized in Table 1. Good to excellent yields of 4-butyl-1,3-dioxolan-2-one (4b) were obtained, with no by-products detected in the experiments (Table 1, entries 1–3). As reported previously,³⁶ pyridine was ineffective under the same conditions (Table 1, entry 4). The effect of the hydroxyl group, therefore the hydrogen bonding ability, is evident in the

reaction between CO_2 and an epoxide, as mentioned previously.^{28-33,36} When **2** and TBAI were used individually, both gave poor yields (Table 1, entries 5 and 6). Thus, the high catalytic activity was realized by the cooperative effect of hydroxypyridines and TBAI.^{28,29,31,36}

Kleij *et al.* worked on the combinations of various phenols and TBAI for the cycloaddition of CO_2 and epoxides in methyl ethyl ketone.²⁹ In their work, simple phenol afforded only 15% yield from **4a** under 10 bar at 45 °C while pyrogallol gave 100% yield (93% isolated yield) under the same condition and 54% yield under 2 bar. Comparing with the present result of **2** (95% isolated yield under 1 atm and 40 °C; Table 1, entry 2), the solvent-free system seems effective for the phenol–TBAI system. In fact we found both phenol and pyrogallol gave comparable or surpassing yield (97% isolated yield) under the present conditions, that is in combination TBAI with no solvent (entries 12 & 13).

On the other hand, Shi *et al.* studied the effect of *p*-methoxyphenol combined with several bases and found that high yield of 98% is achieved with *N*,*N*-dimethylaminopyridine (DMAP) under high CO₂ pressure and temperature (3.57 MPa, 120 °C) but only 20% is obtained using pyridine.³³ It is also interesting that they observed *p*-toluenesulfonic acid, much stronger acid, and DMAP gave poor yield of 10% under the same condition. We tried the combination of **2** and DMAP to obtain almost no carbonate (Table 1, entry 7). Under the present reaction conditions (1 atm CO₂, 40 °C), **2** works very efficiently in combination with TBAI.

1 able 1. Reaction of 1,2-cpoxylicxane with CO ₂ using various catalysis	Table 1	. Reaction of	1,2-epoxyhex	ane with CO_2	using	various	catalysts ^a
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	ⁿ Bu 4a Co ₂ Catalyst	nBu 4b	
Entry	Catalyst	Co-catalyst	Yield ^b (%)
1	1	ⁿ Bu ₄ NI	67
2	2	ⁿ Bu ₄ NI	95
3	3	ⁿ Bu ₄ NI	86
4	pyridine	ⁿ Bu ₄ NI	10
5	2	-	6
6	-	ⁿ Bu ₄ NI	9
7	2	DMAP	0
8	2-methyl-3-hydroxypyridine	ⁿ Bu ₄ NI	95
9	2,4-dimethyl-3-hydroxypyridine	ⁿ Bu ₄ NI	83
10	2	ⁿ Bu ₄ NBr	82
11	2	ⁿ Bu ₄ NCl	36
12	phenol	ⁿ Bu₄NI	<mark>97</mark>
13	pyrogallol	ⁿ Bu₄NI	<mark>97</mark>

^a *Reaction conditions*: **4a** (5.0 mmol), 40 °C, CO₂ (1 atm), 24 h, Catalyst (5.0 mol%), Tetrabutylammonium halide (5.0 mol%), Solvent-free. ^b Isolated product obtained after chromatographic purification.



Figure 1. Comparative kinetics in the formation of **4b** from **4a** and CO₂ using **1–3** as catalysts. Reaction conditions: **4a** (5.0 mmol), CO₂ (1 atm), catalyst (5.0 mol%), TBAI (5.0 mol%), 40 °C.

Interestingly, the reaction yield varied depending on the structure of the hydroxypyridine: **2** afforded the best result, followed by **3** and then **1** (Table 1, entries 1–3). To study the intrinsic catalytic activity in detail, kinetic studies of the catalytic conversion of CO₂ and **4a** to **4b** were carried out using **1**, **2**, or **3** and TBAI as co-catalysts for 4 h. The resulting kinetic curves of three different catalysts are shown in Figure 1 and summarized in Table S1. Catalyst **2** showed the highest catalytic activity, with reaction rates in the order **2** > **3** > **1**, affording the TON of 7.8 for **2** in the initial 2 h while those of **1** and **3** were 1.5 and 3.3, respectively. Such a difference can be explained from the acidity of their hydroxyl groups. Shi *et al.* reported that this reaction was catalyzed well by phenols with pK_a s between 7.15 and 10.64.³³ The pK_a of **2** meets this acidity requirement (Scheme 2),⁴⁵ which is a principal reason that **2** afforded the highest yield. It is known that **1** and **3** tautomerize to the corresponding pyridones **1'** and **3'** (Scheme S1),⁴⁶ which lowers their acidity and therefore the catalytic ability of the hydroxyl groups.³² It is still interesting that weaker acids, **1** and **3** with pK_a values higher than 11, have good catalytic activities. The tautomer forms containg the NH structure might contribute the reaction more or less.

Two kinds of methylated 3-hydroxypyridines were studied to further study the effect of hydroxyl group. While 2-methyl-3-hydroxypyridine afforded the same high yield (95%) as **2** (Table 1, entry 8), the yield of the product (83%) became lower more than 10% by 2,4-dimethyl-3-hydroxypyridine (entry 9). The results clearly suggest the importance of hydrogen bonding of the hydroxy group; steric hindrance of the methyl groups introduced at 2- and 4-positions of **2** disturbs the hydroxy group in formation of a hydrogen bond with the epoxide.

2.2 Optimization of the reaction conditions

In the synthesis of cyclic carbonates from CO₂ and epoxides, it has often been proposed that the halide ion opens the activated epoxide ring through a nucleophilic reaction.^{30,34-36,47,48} In order to study the effect of the halide ion, tetra-*n*-butylammonium bromide (TBAB) and tetra-*n*-butylammonium chloride (TBAC) were used in combination with **2**; the results were also summarized in Table 1. The activity of the catalysts increased in the order: TBAC < TBAB < TBAI (entries 2, 10, and 11), however this is inconsistent with the order of nucleophilicity of halide anions (Cl⁻ > Br⁻ > I⁻), which has been observed in some systems.^{30,47} It is probable that the activity is corresponding with leaving ability of the halide ions (Cl⁻ < Br⁻ < I⁻), as noted previously.^{30,34-36,48}



Figure 2. Effect of the amount of **2**/TBAI (1:1) on the yield of **4b**. Reaction conditions: **4a** (5.0 mmol), CO₂ (1 atm), **2** (1.0–5.0 mol%), TBAI (1.0–5.0 mol%), 24 h, 40 °C.

The effect of amount of the binary catalyst 2 and TBAI (1:1) was evaluated, with the results shown in Figure 2. Even when the catalyst loading was reduced to 1 mol%, the yield of 4b was as high as 71%, demonstrating the high capability of this catalytic system. Catalytic activity gradually increased with the catalyst amount, and the yield increased to 94% using a 4 mol% catalyst loading.



Figure 3. Time dependence of the synthesis of **4b** by **2**/TBAI. Reaction conditions: **4a** (5.0 mmol), 40 °C, CO₂ (1 atm), **2** (5.0 mol%), TBAI (5.0 mol%).

The reaction time course was also examined at 40 °C with a 5 mol% loading of 2/TBAI, with the results shown in Figure 3. The reaction proceeded quickly in the first few hours, then gradually slowed, to afford a 95% yield after 24 h. The effect of reaction temperature was studied and summarized in Table S2. It was shown that the yield substantially increased with increase of the reaction temperature from 25 to 40 °C, whereas there seemed minor increase in catalytic activity at 60 °C.

2.2. Cycloaddition of CO₂ to various epoxides

According to the results mentioned above, cycloaddition reactions of CO_2 with various epoxides in the presence of 2/TBAI (5 mol%) were studied under atmospheric pressure and at 25–60 °C depending on the reactivity of the epoxide; the results are summarized in Table 2. All products are known and the analytical data match those for the compounds prepared in the earlier study.^{36,40} The catalytic system effectively converted mono-substituted aliphatic epoxides into the corresponding cyclic carbonates in yields of 82–96% at 25 °C without solvent (Table 2, entries 1–6). In entry 5, product precipitation lowered the yield by preventing continuous stirring of the reaction mixture. Epoxides with longer alkyl groups gave slightly lower yields (Table 2, entries 6 and 7), which could be improved (>90%) at higher temperatures (40 °C). The relatively low yield using styrene oxide at 40 °C was probably due to the presence of the aromatic ring, which makes the ring-opening step more favorable on C_{α} (most substituted carbon), unlike the apparent preference for C_{β} (least substituted carbon) observed for other epoxides (Table 2, entries 1–7), resulting in a less nucleophilic alkoxide intermediate, which causes CO_2 activation (insertion) to be kinetically more difficult than for aliphatic epoxides.⁴⁹ Thus, a higher temperature (60 °C) was necessary to achieve a 95% yield. Cyclohexene oxide exhibited the lowest reactivity, even at 60 °C (Table 2, entry 9), probably owing to the greater steric hindrance compared with monosubstituted epoxides.²⁸

This catalytic system was also applied for the coupling reaction of enantiomerically pure epoxides and CO_2 . When (*S*)-styrene oxide was transformed to the corresponding carbonates, the ee value of the carbonate was 92% ee at 40 °C and it lowered to 84% ee at 60 °C (Table 2, entry 10). On the other hand, unexpectedly, further decrease to 64% ee was observed for (*R*)-glycidyl benzyl ether even at 40 °C (entry 11), which demands further refinement of the present system in the next stage.

 Entry	Epoxide	Product	Yield ^b (%)	
1	CI	CI-	96	
2			93	R
3			91	<u>S</u>
4		ý J	86	
5	Ph	Ph	82	
6		о H ₃ C-() ₅	82 91°	
7	n _{Bu}	nBu O	78 95°	
8	Ph	Ph	86° 95 ^d	
9	o		14 ^d	
<mark>10</mark>	Ph ^{vi}	Ph	84 ^c (92% ee) 93 ^d (84% ee)	
 11	Ph-/	Ph-O-V	<mark>89° (64% <i>ee</i>)</mark>	

Table 2. Reactions of various epoxides with CO_2 using **2** as catalyst and TBAI as co-catalyst^a.

^a *Reaction conditions*: Epoxide (5.0 mmol), CO₂ (1 atm), **2** (5.0 mol%), TBAI (5.0 mol%), solvent-free, 24 h, 25 °C. ^b Isolated product obtained after chromatographic purification. ^c 40 °C. ^d 60 °C.

2.3. Effect of water and other gas components in CO₂

The ultimate goal of this research was the direct fixation of CO_2 in combustion gases, which can contain other gas components, including water. Under such conditions, other gas components could affect the reaction and/or catalytic system. For practical applications, it is important to study the effect of water and other gas components on the present system.

First, the effect of H_2O on the 2/TBAI catalytic system was studied using 4a in the presence of H_2O (1–5 mmol). As shown in Figure 4, the yield was unaffected by addition of a small amount of water up to the amount of the substrate and 20 times more than the catalyst. Moisture in the feed gas, therefore, does not appear to impair the application of this catalytic system to fix CO_2 gas at 40 °C under 1 atm of CO_2 .



Figure 4. Effect of water on the catalytic activity of **2**/TBAI for the synthesis of **4b**. Reaction conditions: **4a** (5.0 mmol), CO₂ (1 atm), **2** (5.0 mol%), TBAI (5.0 mol%), H₂O (variable), 24 h, 40 °C.



Figure 5. Effect of CO₂ purity in feed gas (CO₂/N₂) on catalytic activity for the synthesis of **4b**. Reaction conditions: **4a** (5.0 mmol), gas mixture (1 atm), **2** (5.0 mol%), TBAI (5.0 mol%), 24 h, 40 °C. CO₂ purities were 9.93%, 39.9%, 67.1%, and >99.99% (CO₂/N₂, v/v). See text for data of 93% pure CO₂.



Figure 6. Effect of a minor component in CO₂ on the catalytic activity of **2**/TBAI for **4b** synthesis. Reaction conditions: **4a** (5.0 mmol), CO₂/minor gas (93/7 (v/v); 1 atm), **2** (5.0 mol%), TBAI (5.0 mol%), 24 h, 40 °C; the minor gas is air, N₂ or O₂.

In most studies, highly pure CO₂ (>99%) was used for the cycloaddition reaction with epoxides. The content of CO₂ in the feed gas is an important factor in practical applications, and the effect of a second gas component was investigated using CO₂/N₂ mixtures with various CO₂ volume fractions (9.93%, 39.9%, 67.1%, and >99%). As shown in Figure 5 and Table S3, the yield of carbonate increased with the increase of CO₂ content. On the other hand, it was also found that prolonged reaction time was not such effective (Table S3, Entries 1 and 5 vs. 2 and 6). It is partly because light sensitive TBAI decomposed during the reaction. In fact the reaction in the dark improved the yield more (Entries 3 & 7).

In order to gain a deeper insight into the effect of a second gas component, O_2 or air (7%, v/v) was added to CO_2 . Figure 6 shows that the yields were not affected by O_2 or air, indicating that these minor components do not deteriorate the reaction. These results mean that the catalytic system has good resistance to oxidation in the presence of up to 7% O_2 . To check the reliability of the manual mixing method for air and O_2 , the same procedure was also applied to N_2 (7%, v/v; Figures 5 and 6).

3. Conclusions

A new efficient catalytic system (3-hydroxypyridine, 2/tetra-*n*-butylammonium iodide) was presented for the synthesis of cyclic carbonates by coupling CO₂ with epoxides without solvent, under atmospheric pressure, and at low to moderate temperatures, 25–60 °C. The effects of hydroxyl group, the p*Ka* and hydrogen bonding ability, were discussed by comparing 2-hydroxypyridine, 4-hydroxypyridine, and 2,4-dimethyl-3 hydroxypyridine: catalytic activity was significantly influenced by the acidity and the steric environment of its vicinity. Moreover, the organocatalytic system exhibited excellent stability in the cycloaddition reaction of CO₂ with epoxides, even in the presence of minor non-toxic components such as water, air and O_2 . This highly active and stable organocatalytic system is expected to provide practical applications for CO_2 fixation.

4. Experimental

All commercially available starting materials and solvents were purchased and used as received, unless stated otherwise. Carbon dioxide (99.99% pure) and CO_2-N_2 mixtures (CO₂ purities: 67.1%, 39.9%, and 9.93%) were used as received without further purification and drying prior to use (Tokyo Koatsu Yamazaki Co. Ltd.). The purities of N₂ and O₂ were 99.9% and 99.5%, respectively.

In order to prepare the mixtures of CO₂ (93 ± 2%, v/v) with N₂, O₂ or air (7 ± 2%, v/v), the minor gas component was introduced into the balloon *via* syringe, as follows: pure CO₂, N₂ and O₂ were introduced into separate balloons (~4.2 L). Then, 300 mL of CO₂ was removed from the CO₂ balloon and 300 mL of N₂ or O₂ taken from the corresponding balloon were introduced into the CO₂ balloon *via* syringe. Ambient air was also introduced into the CO₂ balloon in the same way.

Reactions were monitored using thin-layer chromatography using 0.25-mm E. Merck silica gel coated on aluminum plates (60F-254). Chemical yields refer to the pure isolated carbonate.

¹H and ¹³C NMR spectra were recorded on Bruker AV-300 or AV-500 spectrometers. The chemical shifts of the products were reported in ppm with reference to Me₄Si as the internal standard in CD₃OD.

4.1. General procedure for the synthesis of cyclic carbonates from CO₂ and epoxides

A 5 mL Schlenk flask was charged with epoxide (5 mmol), hydroxypyridine (0.25 mmol), and tetrabutylammonium halide (0.25 mmol), and a CO₂ balloon (20 cm of diameter) was connected to the flask (1 atm). The total volume of the gas phase, including the connection, was approx. 4.2 L. The reaction mixture was set to the relevant temperature and stirred for 24 h. The reaction mixture was allowed to cool to room temperature and the product was isolated by silica gel column chromatography using a mixture of hexane and ethyl acetate (1:1–2:1, v/v) as an eluent.

In order to examine the effect of water on catalytic activity, the above procedure was used, but with the known amounts of distilled water added into the reactor.

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