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# Efficient and practical organocatalytic system for the synthesis of cyclic carbonates from carbon dioxide and epoxides: 3-hydroxypyridine/tetra-*n*-butylammonium iodide

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ABSTRACT

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 $CO_2$, 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 $CO_2$ and $N_2$ in various ratios indicated that the yield depends on $CO_2$ content, due to the solubility of $CO_2$ in the reaction mixture. The system was also shown not to be deteorated by the presence of $H_2O$, air or $O_2$.

## 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 groups[35] 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 $CO_2$ 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

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conditions such as solvent-free, atmospheric pressure of $CO_2$, moderate temperature (Scheme 1).

## 2. Results and discussion

### 2.1. Reaction with hydroxypyridine–TBAI systems

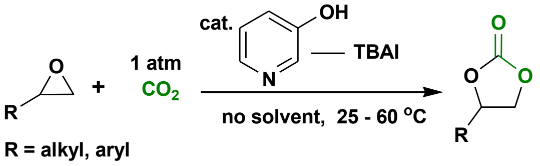
Although the application of various organic bases to $CO_2$ activation or absorption has been reported,[39–44] we have shown that pyridine is not a good catalyst for the cycloaddition of $CO_2$ and epoxides in the presence of TBAI at ambient pressure.[36] However, as mentioned above, hydroxy groups are 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.

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 $CO_2$ 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]

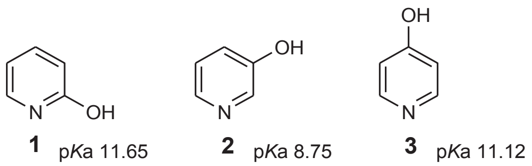
Kleij et al. worked on the combinations of various phenols and TBAI for the cycloaddition of $CO_2$ and epoxides in methyl ethyl ketone.[29] In their work, simple phenol afforded only 15% yield from **4a** under 10 bar at 45 °C while pyrogallol gave 100% yield (93% isolated yield) under the same condition 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 $CO_2$ 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 $CO_2$, 40 °C), **2** works very efficiently in combination with TBAI.

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 $CO_2$ 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 Fig. 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



**Scheme 1.** Synthesis of cyclic carbonates from $CO_2$ and epoxides.



**Scheme 2.** Structures of hydroxypyridines and p*Ka* values of the hydroxy groups.

**Table 1**
Reaction of 1,2-epoxyhexane with $CO_2$ using various catalysts.[a]

| Entry | Catalyst | Co-catalyst | Yield[b] (%) |
|---|---|---|---|
| 1 | **1** | $^nBu_4NI$ | 67 |
| 2 | **2** | $^nBu_4NI$ | 95 |
| 3 | **3** | $^nBu_4NI$ | 86 |
| 4 | pyridine | $^nBu_4NI$ | 10 |
| 5 | **2** | – | 6 |
| 6 | – | $^nBu_4NI$ | 9 |
| 7 | **2** | DMAP | 0 |
| 8 | 2-methyl-3-hydroxypyridine | $^nBu_4NI$ | 95 |
| 9 | 2,4-dimethyl-3-hydroxypyridine | $^nBu_4NI$ | 83 |
| 10 | **2** | $^nBu_4NBr$ | 82 |
| 11 | **2** | $^nBu_4NCl$ | 36 |
| 12 | phenol | $^nBu_4NI$ | 97 |
| 13 | pyrogallol | $^nBu_4NI$ | 97 |

[a] *Reaction conditions*: **4a** (5.0 mmol), 40 °C, $CO_2$ (1 atm), 24 h, Catalyst (5.0 mol%), Tetrabutylammonium halide (5.0 mol%), Solvent-free.

[b] Isolated product obtained after chromatographic purification.

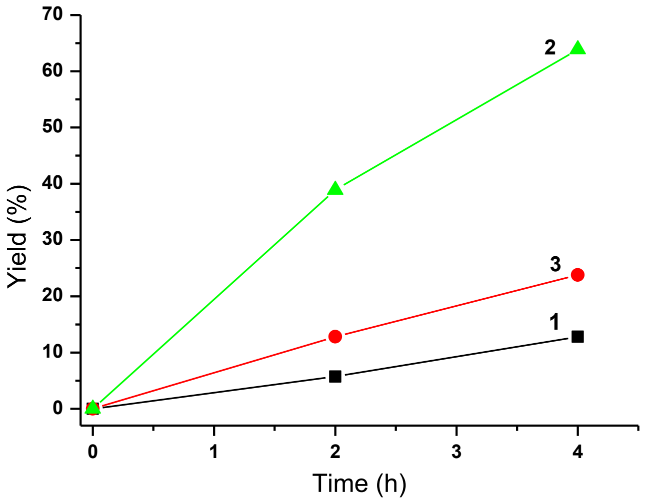


**Fig. 1.** Comparative kinetics in the formation of **4b** from **4a** and $CO_2$ using **1**–**3** as catalysts. Reaction conditions: **4a** (5.0 mmol), $CO_2$ (1 atm), catalyst (5.0 mol%), TBAI (5.0 mol%), 40 °C.