Cycloaddition of Carbon Dioxide and Epoxides using TRIS and Halides as Dual Catalyst System

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Abstract: Hydroxyl-containing organocatalysts, e.g. TRIS (Tris(hydroxymethyl)aminomethane) in combination with halide anion such as tetrabutylammonium iodide (TBAI) were demonstrated to be efficient catalyst systems for the synthesis of cyclic carbonates from CO_2 in excellent yield and selectivity under solvent-free conditions. With 1.0 mol% catalyst loading, 96% SC yield with 99% conversion were obtained at 110 ℃ and 2.0 MPa for 6.0 h of reaction. Interaction of multi hydroxyl group in TRIS with the epoxide via hydrogen bonding presumably facilitates the ring-opening of the epoxide by the nucleophile e.g. iodide.

Keywords: Carbon Dioxide, Cyclic Carbonate, Hydrogen Bonding.

1. Introduction

Chemical conversion of carbon dioxide into cyclic carbonate has attracted much attention in recent years because CO_2 is not only a renewable, abundant and nontoxic resource but also a primary greenhouse gas responsible for climate change. Five-membered cyclic carbonates, which is produced by cycloaddition reaction of CO_2 to epoxides, can be regarede as an important contribution from the viewpoint of resource utilization. They can be used as electrolytes for Li-battery, aprotic polar solvents and fuel additives. For the synthesis of cyclic carbonates, various catalysts including heterogeneous (supported catalysts i.e. graphene oxide[1], SBA-15[2]) and homogeneous catalysts (i.e. quaternary ammonium salts[3] and ionic liquid[4]) have been developed so far. Their benefits are eliminating phosgene as a reagent, and also being 100% atom economical. In addition, the reactions are carried out under solvent-free conditions. Recently, several efficient dual catalyst systems have been developed, such as a mixture of hydrogen-bond donors (HBDs), due to their properties to activate epoxides and further facilitate the reaction with CO_2. Pyrogallol, pentaerythritol, chitosan and cellulose are several phenolic and polyhydroxy compounds that had been successfully being employed as the source of HBDs[5]. We recently reported that aminopropyl-fucntionalized graphene oxide (AP-GO) catalyzed the synthesis of cyclic carbonates with co-catalysts [6].

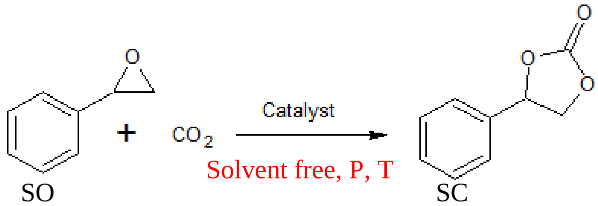
Based on the success of dual catalyst system with HBDs as one of their compounds, we designed a new dual catalyst system, metal- and solvent-free that consists of HBDs as the main catalyst and halides salts as co-catalyst affording five-membered cyclic carbonates. Herein, Tris(hydroxymethyl)aminomethane (TRIS) which is commercially available was selected as co-catalyst due to the excellent HBD that could be used synergistically with halide salts as dual activation for the ring-opening process of epoxide.

2. Experimental

CO_2 with purity of 99.99% was commercially available. All the organic chemicals, solvents and reagents were purchased from Sigma Aldrich, Nucalai Tesque, Kanto Chemical, TCI, WAKO from commercial suppliers, Japan, were used without further purification/pre-treatment. The products were confirmed by GC-17A Shimatsu using FID detector and DB-FFAP capillary column. All the coupling reactions were conducted in a 30 mL stainless steel autoclave reactor.

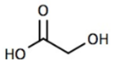
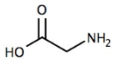
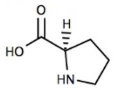
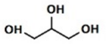
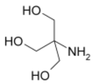
3. Results and discussion

The reaction of styrene oxide (SO) with CO_2 to produce styrene carbonate (SC) under solvent-free condition (Scheme 1) was used as the model reaction to study the effect of various parameters on the reaction outcome (Table 1). From our previous result, we found that tetrabutylammonium has an important role in cycloaddition reaction (Table 1, entries 1-3). Herein, tetrabutylammonium was used as co-catalyst to examine the effect of functional groups in several reported HBD's. Instead of TBAI, previously reported results used another main catalyst such as TBABr and KI. After the initial screening on several reported HBDs (Table 1, entries 4-8), we selected TRIS as the catalyst since the glycerol (Table 1, entry 9) which has a similar number of hydroxyl groups produced little results, whereas the proposed combination of TBAI and TRIS produced the highest synergetic activity. Although the TRIS alone was incapable of producing any catalytic activity.



Scheme 1. Reaction of styrene oxide (SO) with CO_2 to produce styrene carbonate (SC) under solvent-free condition.

Table 1. Effect of HBD's type as epoxide activator on the conversion of styrene oxide.[a]

No.	Co-catalyst	catalyst		SO Conv. (%)[b]	SC yield. (%)[b]	SC Select. (%)[b]
1[6]	TBAI	AP-GO		95	94	99
2[1]	TBACl	None		99	94	99
3	TBAI	None		38	37	96
4	TBAI	Butyraldehyde		62	57	93
5	TBAI	Acetic acid		84	81	97
6	TBAI	Glycolic acid		94	86	92
7	TBAI	Glycine		60	54	89
8	TBAI	L-Proline		92	85	93
9	TBAI	Glycerol		97	89	92
10	None	TRIS		0	0	0
11	TBAI	TRIS		99	96	97

Reaction condition :[a] each catalyst : 0.05 mmol (1:1), SO : 5 mmol, 2 MPa of CO_2 (30 mL of stainless autoclave), 110 °C, 6h. [b] Determined by GC, main by product is 1-phenyl-1 2-ethanediol.

The effects of various parameters, such as co-catalyst ratio, catalyst amount, reaction time, temperature and CO_2 pressure on the reaction were investigated. NMR measurements were achieved to monitor hydrogen bonding among reactants, which will be shown in the presentation.

4. Conclusions

We have demonstrated that the cycloaddition of carbon dioxide with epoxide could be effectively carried out using a new dual catalyst system (TRIS/TBAI) owing to synergistic effects of multi-hydroxyl groups of TRIS and iodide anion. In the presence of TRIS, this catalyst activity was greatly activated the epoxide in comparison to mono-hydroxyl group without any amino group in the structure. Ratio TRIS/TBAI 1:1, 1 mol% catalyst loading, 2 MPa of CO_2, 110 °C and 6 h were found to optimum condition for the synthesis of styrene carbonate.

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