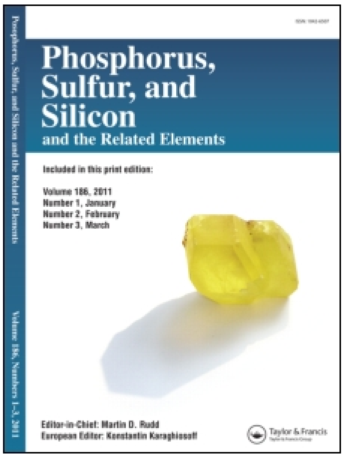

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Jie-Sheng Tian[a]; Fei Cai[a]; Jian-Quan Wang[a]; Ya Du[a]; Liang-Nian He[a]
[a] State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, P. R. China

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Environmentally Benign Chemical Conversion of CO_2 into Organic Carbonates Catalyzed by Phosphonium Salts

Jie-Sheng Tian, Fei Cai, Jian-Quan Wang, Ya Du, and Liang-Nian He
State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China

Quaternary phosphonium salts were proved efficient homogeneous catalysts for solvent-free synthesis of cyclic carbonates from carbon dioxide and epoxides. Propylene carbonate was produced in quantitative yield and excellent selectivity. Furthermore, a PEG-supported phosphonium salt was solidified by adding ether and cooling after reaction and recovered by a simple filtration. Hence immobilization of a phosphonium salt on PEG provides an alternative pathway for realizing homogeneous catalyst recycling.

Keywords Carbon dioxide; cyclic carbonate; homogeneous catalyst; phosphonium salt

INTRODUCTION

In recent years, chemical fixation of CO_2 into industrially useful materials has attracted much attention from the standpoint of the protection of environment and natural resource utilization.[1,2] One promising methodology in chemical CO_2 fixation is the synthesis of cyclic carbonates from CO_2 and epoxides. These cyclic carbonates are widely used for various purposes, for instance, aprotic polar solvents, fine chemical intermediates, electrolytic elements of lithium secondary batteries, sources for polymer and engineering plastic syntheses, and ingredients for pharmaceutical/fine chemicals in biomedical applications.[3,4,7]

Various homogeneous and heterogeneous catalysts[5–13] are explored for the synthesis of cyclic carbonates from CO_2 and epoxides. As for

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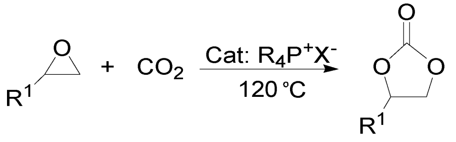
Address correspondence to Liang-Nian He, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China. E-mail: heln@nankai.edu.cn

the heterogeneous catalysts, they have the advantages of easy product purification and catalyst recovery at the separation stage of a process. But heterogeneous catalysts in general have poor reactivity, such as, polymer-supported quaternary onium salts,[5,6] silica-supported quaternary ammonium salts,[7] and silica-supported ionic liquids,[8] Cs-P-Si oxide,[9] and the like. Though homogeneous catalysts,[10–12] such as Et_4NBr, which are often employed in current industrial processes, offer many advantages including high activity and selectivity, it is undesirably dissolved in a phase containing cyclic carbonate. Consequently, it is necessary to separate the catalyst from the product through a purification process, e.g., distillation after completion of the reaction, thus resulting in complicated production processes, and decomposition of the catalyst or formation of by-products during the separation step. As a consequence, the development of a more efficient and environmentally benign process for cyclic carbonate synthesis along with homogeneous catalyst recycling still remains a challenging issue. In order to improve the catalytic activity and facilitate the separation of the catalyst, our strategy is a so-called "monophase reaction, biphasic separation" (Figure 1) one, such that supporting active homogenous catalyst e.g. phosphoniun halide, which could be easily detected by ^{31}P NMR, onto CO_2-philic polymer is expected to enhance the catalytic activity and recover the catalyst.

Herein, we would like to report an efficient and environmentally benign process for a highly selective synthesis of cyclic carbonates from supercritical carbon dioxide and epoxides catalyzed by quaternary phosphonium salts, as shown in Scheme 1. An almost quantitative yield together with excellent selectivity was attained. Furthermore, the catalyst was found to be applied to a variety of terminal epoixdes, forming the corresponding cyclic carbonates.



$R^1 = CH_3$, $^iPrOCH_2$, Ph, $PhOCH_2$, CH_2Cl

$R_4P^+X^-$ (Cat.): R = alkyl, Ph, PEG

X = Cl, Br

SCHEME 1 Synthesis of various carbonates catalyzed by quaternary phosphonium salts.

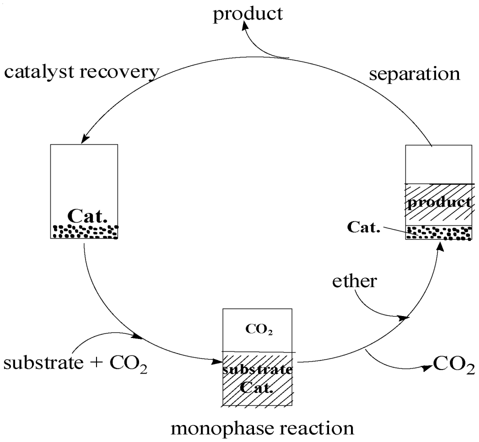


FIGURE 1 "Monophase reaction, biphasic separation" for catalyst recycling.

RESULTS AND DISCUSSION

In the framework of our continuous effort on developing the simple and efficient route to organic carbonates,[5,7,8,14–16] such as cyclic carbonate and dimethyl carbonate starting from CO_2, we designed and synthesized a series of quaternary phosphonium salts for the synthesis of cyclic carbonates from CO_2 and epoxides.

The carboxylation of propylene oxide with CO_2 to propylene carbonate in the presence of 1 mmol% of quaternary phosphonium salts was conducted in a batch wise operation under various conditions as shown in Table I. As expected, phosphonium salt (n-Bu_4PBr)

TABLE I Synthesis of Propylene Carbonate from Propylene Oxide and CO_2 Catalyzed by Quaternary Phosphonium Salts[a]

Entry	Cat.	P/MPa	t/h	T/ K	PC[b] Yield/%
1	Et_4NBr	8	10	423	94
2	n-Bu_4NBr	8	10	423	95
3	PEG_{2000}	8	6	393	0
4	Ph_3PBuBr	8	6	393	62
5	n-Bu_4PBr	8	6	393	80
6	n-Bu_4PBr/ PEG_{2000}	8	6	393	90
7	n-$Bu_3PC_{12}H_{25}Br$	8	6	393	99
8	$PEG_{2000}(PPh_3Br)_2$	8	6	393	80
9	$PEG_{2000}(PBu_3Br)_2$	8	6	393	99
10	$PEG_{2000}(NBu_3Br)_2$	8	6	393	99

[a]Reaction conditions = propylene oxide, 28.6 mmol (2 ml); cat., 1 mol %; [b]PC = propylene carbonate.

exhibited a moderate catalytic activity (Table I, entry 5) under supercritical conditions (393 K, 8 MPa, 6 h). Notably, the order of the catalytic activity among quaternary phosphonium salts was found to be $PEG_{2000}(PBu_3Br)_2 \approx n\text{-}Bu_3PC_{12}H_{25}Br > PEG_{2000}(PPh_3Br)_2 \approx n\text{-}Bu_4PBr > Ph_3PBuBr$, while the selectivity remained over 98% for all the cases (Table I, entries 4–5, 7–9). As a result, the catalytic activity is influenced by the substituents on the phosphorus atom, which could presumably be responsible for the electrophilic reactivity of the phosphonium cation and nucleophilicity of the counter-anion bromide.

Though PEG_{2000} itself was inactive (Table I, entry 3), PEG-supported phosphonium salt, e.g,. $PEG_{2000}(PBu_3Br)_2$ displayed higher catalytic activity than the unsupported salt (n-Bu_4PBr), and was even more effective than the simple physical mixture of n-Bu_4PBr and PEG_{2000} under the same conditions (Table I, entries 5, 6, 9). Accordingly, the phosphonium salts can be considered as the active species for the reaction, and supporting n-Bu_4PBr on soluble polymer (PEG_{2000}) improves the catalytic activity. The enhancement of catalyst performance by supporting n-Bu_4PBr on soluble PEG is presumably attributed to the benefits from changes in the physical properties of the reaction mixture, such as lower melting points, lower viscosity, high diffusion rates, and increased solubility for propylene oxide and CO_2 through the CO_2-expansion of a liquid effect.[15,16] Obviously, $PEG_{2000}(PBu_3Br)_2$ displayed higher catalytic activity and lower reaction conditions than Et_4NBr, n-Bu_4NBr (Table I, entries 1–2, 9), which are often employed in current industrial processes. Notably, in comparison with a PEG-supported ammonium salt (entries 9 vs. 10), $PEG_{2000}(PBu_3Br)_2$ has a distinct advantage of easily being detected by ^{31}P NMR.

In conclusion, phosphonium salts were shown to be excellent activity towards the synthesis of cyclic carbonates. Furthermore, a PEG-supported phosphonium salt as homogeneous catalyst was readily separated and reused. Further development of novel quaternary phosphonium salts for chemical fixation of CO_2 into organic carbonates is still under investigation in our laboratory.

EXPERIMENTAL

Chemical Reagents

Carbon dioxide with a purity of 99.99% was commercially available, and epoxides were supplied from Aldrich Company. Other reagents were of analytical grade and used as received.

Typical Procedure for the Cycloaddition Reaction

The experiment was carried out in a stainless-steel autoclave reactor with an inner volume of 25 ml. A typical procedure was as follows: propylene oxide (28.6 mmol), and catalyst (1 mol %), and biphenyl (80 mg, an internal standard for GC analysis) were charged in an autoclave under nitrogen at r. t. Then CO_2 (gas, ca. 3.0 MPa) was introduced to the above reactor. The autoclave was heated in an oil bath. The initial pressure was adjusted to 8 MPa at 393 K. After cooling, the products were analyzed by gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5, 30m × 0.25 μm) using a flame ionization detector, and further identified using GC-MS (HP G1800A) by comparing retention times and fragmentation patterns with those of authentic samples. The products were also characterized by NMR. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-plus 400 spectrometer. Chemical shifts were given as δ values referenced in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard.

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