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Cationic organobismuth complex as an effective catalyst for conversion of CO₂ into cyclic carbonates

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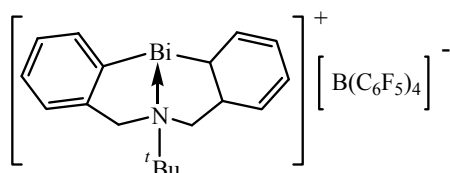
Abstract In order to achieve high-efficiency conversion of CO₂ into valuable chemicals and to exploit new applications of organobismuth compounds, cationic organobismuth complex with 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine framework was the first time examined for the coupling of CO₂ into cyclic carbonates, using terminal epoxides as substrates and tetrabutylammonium halide as co-catalyst in a solvent-free environment under mild conditions. It is shown that the catalyst exhibited high activity and selectivity for the coupling reaction of CO₂ with a wide range of terminal epoxide. The selectivity of propylene carbonates could reach 100%, and the maximum turnover frequency was up to 10,740 h⁻¹ at 120°C and 3 MPa CO₂ pressure when tetrabutylammonium iodide was used as co-catalyst. Moreover, the catalyst is environmentally friendly, resistant to air and water, and can be readily reused and recycled without any loss of activity, demonstrating a potential in industrial application.

Keywords cationic organobismuth complex, terminal epoxide, carbon dioxide, coupling, cyclic carbonate

1 Introduction

CO₂ is a greenhouse gas known to cause global warming. On the other hand, CO₂ is nontoxic, abundant, inexpensive, nonflammable, and highly functional. Much attention has been paid to its chemical fixation [1-2]. One of the most interests is to couple CO₂ with high-energy epoxides for the generation of cyclic carbonates. Five- and six-membered cyclic carbonates are excellent aprotic polar solvents and used extensively as intermediates in the production of fine chemicals, plastics, and pharmaceuticals. In the past decades, a wide range of catalysts have been explored for the generation of cyclic carbonates, including alkali metal salts [3], group III-V metal compounds [4-5], ionic liquids [6-11], onium salts [12-18], and transition metal complexes [19-21], etc. It is noted that there is a recent development of synthesizing cyclic carbonate by means of bi-component catalysts [4-5, 13-15]. Moreover, there are suggestions that the coupling reaction over the bi-component systems proceeds under a dual requirement of Lewis acid and Lewis base sites, for epoxide and CO₂ activation, respectively [5, 7-8, 14, 17-18].

It is of interest and significance to exploit the use of bismuth compounds in CO₂ conversion since bismuth is the only stable heavy element in nature that is very low in toxicity and free of radioactivity. Many Bi compounds have been widely used in catalysis, organic synthesis, and cosmetics industries, etc [22-25]. From the standpoint of “Green Chemistry” and “Sustainable Development”, it is envisaged that Bi compounds will find new applications. Recently, Shimada et al. [25] synthesized a novel and stable cationic three-electron three-coordinate organobismuth complex with 5,6,7,12-Tetrahydrodibenz [c,f][1,5] azabismocine framework ($[{}^t\text{BuN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, denoted as [Bi] hereinafter, whose molecular structure is shown in Scheme 1). The compound exhibits good Lewis acidity and strong coordination ability, and can accept neutral molecules such as aldehydes, methanol, acetonitrile, and dichloromethane. It was predicted that the material could be used as catalyst in organic synthesis. To the best of our knowledge, there has been no report on the use of cationic organobismuth complexes as catalysts for the coupling of CO₂ with epoxide into cyclic carbonates. As a continuation of our works on the use of bismuth compounds as environmentally friendly reagents or catalysts for organic synthesis [24], and with the aim of developing catalysts suitable for chemical fixation of CO₂ onto various epoxides, we synthesized the [Bi] compound according to the method proposed by Shimada et al.[25] and undertook a study on its utilization for CO₂ coupling reaction.



Scheme 1 Molecular structure of the cationic organobismuth compound

2 Experimental

2.1 Chemicals

The reagents and chemicals (analytic grade unless otherwise stated) were purchased from Aldrich Chemical Co. America. Epoxides and all solvents were dried by distillation over CaH_2 or by means of 4A molecular sieve. The CO_2 (99.99% purity) purchased from Changsha Gas Co. China was dehydrated by 4A molecular sieve in a high-pressure stainless-steel tube prior to use. Other chemicals were used as received.

2.2 Cationic organobismuth compound synthesis

The organobismuth compound ($[\text{tBuN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$) was synthesized according to the method proposed by Shimada et al. [25]. Briefly: To a slurry of $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ (20.0 mmol, 13.7g) in 230 ml of CH_2Cl_2 at -20°C was added a cooled (-20°C) solution of bismuth chloride (20.0 mmol, 9.92 g) in 110 ml of CH_2Cl_2 . The mixture was stirred at -20°C for 3 h and then allowed to warm slowly to room temperature. The precipitated LiCl was removed by filtration, and the solvent was removed under vacuum to give the desired compound. After purification by recrystallization in CH_2Cl_2 /hexane, the product appeared in the form of colorless crystals (20.1 g, 88.1 %). Proton and carbon nuclear magnetic resonance (NMR) (Bruker-AV400 (400MHz), Bruker, Switzerland) results showed that they were the desired compounds. ^1H NMR (399.975 MHz, CDCl_3/TMS) δ 1.45 (s, 9H), 4.72 (d, $J = 15.5$ Hz, 2H), 5.01 (d, $J = 15.5$ Hz, 2H), 7.53 (td, $J = 7.5, 1.2$ Hz, 2H), 7.73 (t, $J = 7.5$ Hz, 2H), 7.85 (d, $J = 7.5$ Hz, 2H), 8.11 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (100.584 MHz, CDCl_3/TMS) δ 28.6, 65.7, 66.5, 124.6 (bs), 129.5, 130.3, 132.8, 136.7 (d, $J_{\text{CF}} = 243$ Hz), 138.1, 138.7 (d, $J_{\text{CF}} = 242$ Hz), 148.6 (d, $J_{\text{CF}} = 241$ Hz), 155.2, 184.1.

2.3 Catalytic test

The coupling reactions were carried out in a 150-ml high-pressure stainless-steel autoclave equipped with a magnetic bar and an electrical heater. In a typical run, the reactor was charged with appropriate amount of catalyst, epoxide, and biphenyl (as internal standard for gas chromatography analysis). It was noted that all weighing procedures were conducted in a glove box under an atmosphere of dry argon. After the reactor was injected with CO_2 to a desired pressure, the reaction mixture was heated to a designated temperature and stirred at ca. 800 r/min for 1 h. Then the reactor was cooled to 0°C in an ice-water bath, and the remaining CO_2 and volatile epoxide were released using an aspirator and absorbed in a saturated solution of K_2CO_3 . The resulting mixture was characterized by gas chromatography-mass spectrometry (Hewlett Packard 6890-5973 MSD gas chromatography-mass spectrometry, Agilent, China) and by NMR technique (Bruker-AV400 (400MHz) spectrometer, Bruker, Switzerland) with TMS as internal standard. The products were quantitatively analyzed by a gas chromatography (Hewlett Packard 6890, Agilent, China) equipped with a flame-ionized detector and Rtx-WAX capillary column (30 m \times 0.25 mm \times 0.25 μm).

3 Results and discussion

3.1 Coupling reaction of CO_2 with propylene oxide

Listed in Table 1 are the results of [Bi]-catalyzed coupling reactions using propylene oxide (PO) as model substrate. It can be seen that [Bi] by itself was catalytically inactive and tetrabutylammonium halides (nucleophilic agents) gave a poor propylene carbonate (PC) yield. However, a combined use of [Bi] and tetrabutylammonium halides resulted in marked enhancement of performance: PO conversions and

turnover frequencies (TOF) were in the range of 60.3–97.5% and 4,824–7,800 h⁻¹, respectively, and selectivities to PC were ca. 100%. It was also found that the catalytic activity of [Bi] was dependent on the nature of Bu₄NX (X = Cl, Br, I) and PO conversion increased in the order of Cl << Br < I, consistent with the increasing order of halide nucleophilicity. For comparison, we also checked the outcomes of having bismuth halides and Ph₃Bi in the presence of Bu₄Ni. It is clear that PO conversion over the catalysts could be ranked in the order of Ph₃Bi << BiCl₃ < BiI₃ ≈ BiBr₃ << [Bi], indicating that a proper Lewis acidity or coordination ability of Bi center was essential for the coupling reaction.

Since the “[Bi] + Bu₄Ni” system showed the best activity towards this reaction, we adopted it to investigate the influence of Bu₄Ni/[Bi] molar ratio (denoted as Bu₄Ni/[Bi] hereinafter) on catalytic performance. As shown in Tab. 1, PO conversion and TOF increased with increase of Bu₄Ni/[Bi] (Entries 12 and 13); and with Bu₄Ni/[Bi] up to 1, the increase of PO conversion slowed down (Entries 14 and 15). Especially, the maximum TOF was up to 10,740 h⁻¹.

Table 1 Catalytic performance of Catalysts^a

entry	catalyst	results ^d		
		X _{PO} /%	S _{PC} /%	TOF/h ⁻¹
1	[Bi]	0	0	0
2	[Bi] + Bu ₄ NCl (1:1)	60.3	>99	4,824
3	[Bi] + Bu ₄ NBr (1:1)	90.7	>99	7,256
4	[Bi] + Bu ₄ Ni (1:1)	97.5	>99	7,800
5	Bu ₄ NCl (0.015 mmol)	–	–	–
6	Bu ₄ NBr (0.015 mmol)	1.0	–	–
7	Bu ₄ Ni (0.015 mmol)	1.6	–	–
8 ^b	BiCl ₃ +Bu ₄ Ni (1:1)	16.7	>99	1,336
9 ^b	BiBr ₃ +Bu ₄ Ni (1:1)	23.3	>99	1,864
10 ^b	BiI ₃ +Bu ₄ Ni (1:1)	22.8	>99	1,824
11 ^b	Ph ₃ Bi+ Bu ₄ Ni (1:1)	2.3	–	–
12 ^c	[Bi] + Bu ₄ Ni (1:1)	82.4	>99	9,888
13 ^c	[Bi] + Bu ₄ Ni (1:0.5)	60.3	>99	7,236
14 ^c	[Bi] + Bu ₄ Ni (1:1.5)	86.0	>99	10,320
15 ^c	[Bi] + Bu ₄ Ni (1:2)	89.5	>99	10,740

Notes: ^a Reaction conditions: propylene oxide, 120 mmol; Bi compound, 0.015 mmol; CO₂ pressure, 3 MPa; 120°C; 1 h; the ratio in parentheses represents the molar ratio of Bi to tetra-n-butylammonium halide salt.

^b BiX₃ (X = Cl, Br, I) or Ph₃Bi by itself showed no catalytic activity.

^c Bi compound, 0.01 mmol.

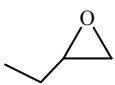
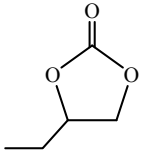

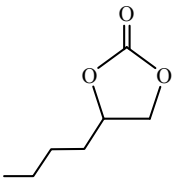
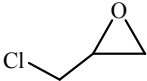
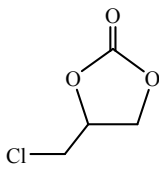
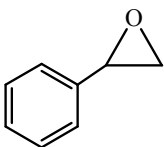
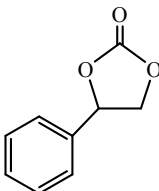
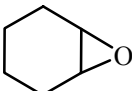
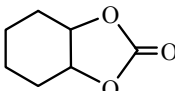
^d GC analysis. X_{PO}: PO conversion; S_{PC}: PC selectivity; TOF: moles of PO converted per mole of Bi per hour.

3.2 Coupling of CO₂ with other epoxides

To confirm the excellent catalytic activity of “[Bi] + Bu₄Ni” catalyst, we selected other five epoxides as substrates to couple with CO₂. As illustrated in Tab. 2, the “[Bi] + Bu₄Ni” system was effective for the coupling of CO₂ with terminal epoxides as well. In all cases the conversions and TOF of epoxides were above 85% and 5,200 h⁻¹, respectively, and selectivity to cyclic carbonates was near 100% under mild conditions (Entries 1–4). With such performances, the catalyst system can be considered as highly suitable for the synthesis of cyclic carbonates from terminal epoxides and CO₂. Shown in Entry 5 is the coupling of CO₂ with cyclohexene oxide (a relatively inert epoxide); TOF was 2,408 h⁻¹ and yield to cyclohexyl-[1,3]-dioxolan-2-one was high.

In addition, the “[Bi] + Bu₄NI” system is resistant to water and air. Comparing to catalysts known to be excellent for catalyzing the coupling reaction, such as zinc halide and imidazolium [6-10], quaternary ammonium [12-16], guanidinium [17], and phosphonium salts [18], the “[Bi] + Bu₄NI” catalyst can be considered as the most active in terms of TOF for the coupling of CO₂ with terminal epoxides.

Table 2 Coupling of CO₂ with terminal epoxides catalyzed by [Bi]⁺Bu₄NI^d

entry	substrate	product	results ^d		
			Conv. /%	Sel. %	TOF/h ⁻¹
1			92.3	>99.0	7,384
2			86.2	>99.0	6,896
3			90.7	>99.0	7,256
4 ^b			87.9	>99.0	5,274
5 ^c			90.3	>99.0	2,408

Notes: ^a Reaction conditions: epoxide 120, mmol; Bi compound, 0.015 mmol; Bu₄NI, 0.015 mmol; initial CO₂ pressure, 3.0 MPa; 1 h (Entries 1–3); 120°C.

^b Reaction time, 80 min.

^c Reaction time, 3 h.

^d GC analysis, Conv.: epoxide conversion; Sel.: cyclic carbonate selectivity; TOF: moles of epoxide converted per mole of Bi per hour.

3.3 Catalyst recycling

To examine the reusability and applicability of the catalyst system, [Bi] and Bu₄NI in 1:1 molar ratio was subject to cycles of PO conversion to PC under reaction conditions similar to those of Tab. 1. Between cycles, separation of liquid product from catalyst was done by distillation under reduced pressure, and the

catalyst was directly reused for the next run. To minimize catalyst loss, the separation processes were conducted over the same autoclave.

As shown in Fig. 1, the decline of PO conversion and PC selectivity was minimal in a test of 8 runs. We also tested the catalyst for six cycles in the coupling of CO₂ with epoxy chloropropane and observed similar efficiency as shown in Fig. 2. Therefore, the catalyst is stable and suitable for reuse.

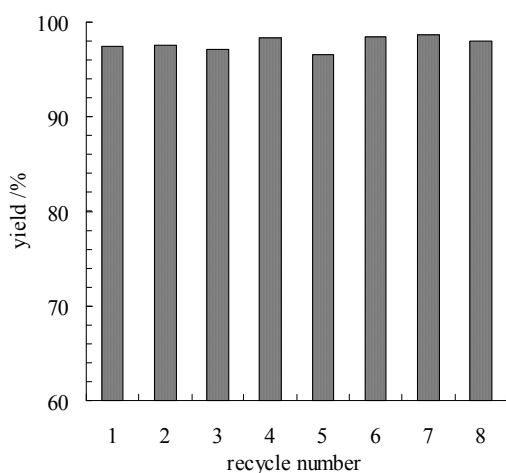


Fig. 1 Catalyst recycling using propylene oxide as substrate (For each cycle: propylene oxide, 120 mmol; Bi compound, 0.015 mmol; Bu₄NI, 0.015 mmol; CO₂ pressure, 3 MPa; 120°C; 1 h.)

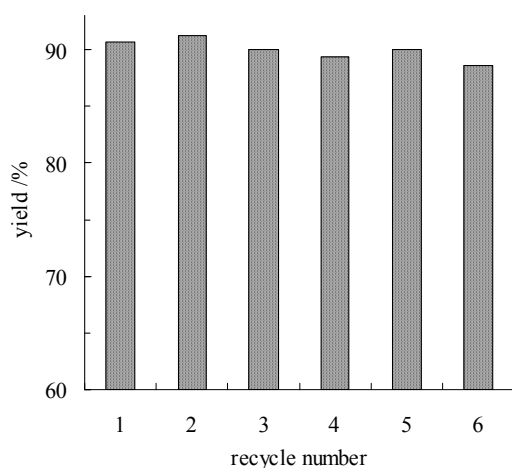
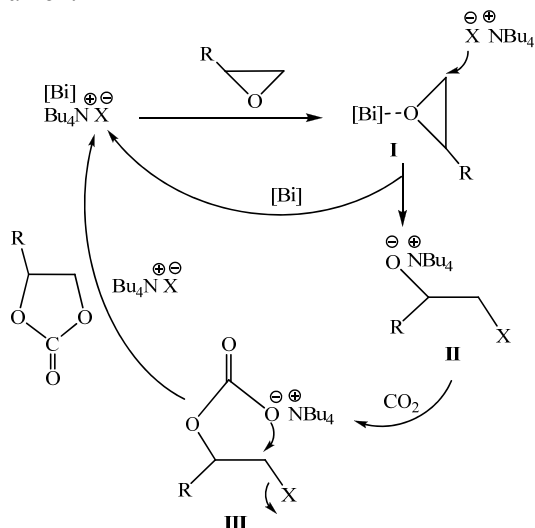


Fig. 2 Catalyst recycling using epoxy chloropropane as substrate (For each cycle: epoxy chloropropane, 120 mmol; Bi compound, 0.015 mmol; Bu₄NI, 0.015 mmol; CO₂ pressure, 3 MPa; 120°C; 1 h.)

3.4 Mechanism consideration

The good catalytic performance of [Bi] + Bu₄NI system bestirred us to investigate the coupling reaction mechanism. Based on the results of references [5, 7-8, 14, 17-18] and those of the present study, we propose a plausible mechanism for the coupling reaction over [Bi] + Bu₄NI (Scheme 2). Since [Bi] has good coordination ability [25], it is envisaged that epoxide coordinates with a [Bi] site of Lewis acid nature to form a [Bi]-epoxide adduct (Complex **I**). As shown in Tab. 1, PO conversion and TOF increased with increase of Bu₄NI/[Bi] ratio when Bu₄NI/[Bi] didn't exceed 1, demonstrating the importance of nucleophilic agent for the coupling reaction. Moreover, many researchers have regarded that the nucleophilic agent is crucial for the ring opening of the epoxide [5, 7-8, 14, 17-18]. In other words, with a nucleophilic agent attacking the less obstructed carbon atom of the coordinated epoxide, there is ring opening and generation of oxy anion (specie **II**). Finally, the insertion of CO₂ into specie **II** would result in the formation of intermediate specie (**III**) that transforms into a cyclic carbonate via intramolecular substitution of halide. Further work is under way to capture and isolate the intermediate species, which will be vital to clarification of the mechanism of the catalytic reaction over [Bi] + Bu₄NI catalyst.

According to the proposed mechanism steps, it is possible to improve catalytic activity by adopting a proper nucleophilic agent or adjusting the coordination ability of Bi center in the cationic organobismuth complex (e.g., by changing the anion or substituted group that bonds to the N atom in the complex). Moreover, it is obvious that the bulky $[B(C_6F_5)_4]^-$ is unfavorable for the coordination of epoxide with a Bi center. Much study is underway to develop new and stable cationic organobismuth complex with small anion.



Scheme 2 A plausible mechanism steps for chemical fixation of CO_2 onto epoxide over $[Bi]^+Bu_4NX$ catalyst

4 Conclusions

In summary, this article reports the first time examples of utilizing cationic organobismuth complex as catalyst for CO_2 conversion. The approach opens up a new dimension in the application of “green” organobismuth complexes. The “[Bi] + Bu_4NI ” system is versatile and robust for the coupling reaction of CO_2 with a wide range of terminal epoxides in a solvent-free environment under mild reaction conditions. The catalyst can be easily separated and reused with little decline in activity and selectivity. The excellent catalytic performance is ascribed to proper Lewis acidity of the cationic organobismuth complex.

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