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Imidazolium zinc tetrahalide-catalyzed coupling reaction of CO_2 and ethylene oxide or propylene oxide

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Abstract

Imidazolium zinc tetrahalides, (1-R-3-methylimidazolium)$_2$ZnX_2Y_2 ($R = CH_3$, C_2H_5, n-C_4H_9, $CH_2C_6H_5$; X = Cl, Br; Y = Cl, Br), prepared by reacting ZnX_2 with (1-R-3-methylimidazolium)Y, were found to have surprisingly high activities for the coupling reaction of CO_2 and ethylene oxide or propylene oxide to produce corresponding cyclic carbonate. The catalytic activity of imidazolium zinc tetrahalide was greatly influenced by the nature of halide groups bonded to the zinc center. The catalytic activity was found in the order of $[ZnBr_4]^{2-} > [ZnBr_2Cl_2]^{2-} \gg [ZnCl_4]^{2-}$. The turnover frequencies (TOF: h^{-1}) increased with increasing temperature, but remained almost unchanged with the increase of pressure.

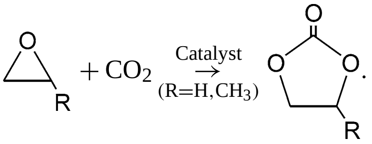
Keywords: Zinc halide; Imidazolium halide; Zinc tetrahalide; Ionic liquid; Ethylene oxide; Propylene oxide; Carbon dioxide; Cyclic carbonate; Ethylene carbonate; Propylene carbonate

1. Introduction

The synthesis of cyclic carbonates by the coupling reactions of epoxides with carbon dioxide has attracted much attention with regard to the utilization of CO_2 [1]. The importance of cyclic carbonates is increased due to their enlarged application—electrolytes in secondary batteries, valuable monomers of polycarbonates and polyurethanes, aprotic polar solvents, and raw materials in a wide range of chemical reactions. Accordingly, substantial literature on catalyst development and mechanistic studies for these coupling reactions exists [2–6]. While the advances have been significant, many areas, such as activity, stability, and recovery of catalysts, still remain to be improved.

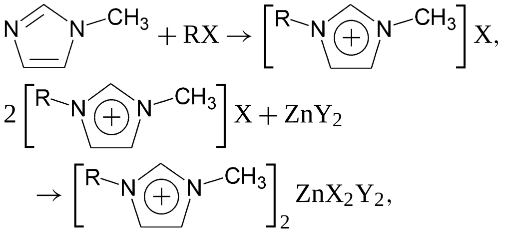
Recently, imidazolium-based ionic liquids have been introduced as effective catalysts for the synthesis of propylene carbonate from the coupling reaction of CO_2 and propylene oxide, but their catalytic activities expressed as turnover frequency (TOF: h^{-1}) were not very high (TOF = 10.63 for [bimim]Cl, 14.98 for [bimim]BF_4 at 110 °C) [7].

We now report that the activities of ionic liquids such as 1-alkyl-3-methylimidazolium halides can be significantly enhanced by the copresence of zinc halides for the coupling reaction of CO_2 with ethylene oxide or propylene oxide as illustrated in



(1)

We also report that the reactions of 1-alkyl-3-methylimidazolium halides with zinc halides produce a series of highly active bis(1-alkyl-3-methylimidazolium) zinc tetrahalide complexes as shown in



(2)

where $R = CH_3$, C_2H_5, n-C_4H_9, $CH_2C_6H_5$; X = Y = Cl, X = Cl, Y = Br; and X = Y = Br.

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2. Methods

2.1. Chemicals

All manipulations were carried out under argon atmosphere unless otherwise stated. Solvents were freshly distilled before use according to the procedure in the literature. Ethylene oxide was purchased from Honam Petrochemical Co. and used as received. Propylene oxide, 1-methylimidazole, and zinc halides were purchased from Aldrich Chemical Co. and used without further purification. CO_2 were purchased from Sin Yang gas. The 1-R-3-methylimidazolium halides were prepared according to the procedure in the literature [8].

2.2. Synthesis of imidazolium zinc tetrahalides

For the synthesis of (1,3-dimethylimidazolium)$_2$ZnBr$_2$Cl$_2$, (**1b**), a solution of (1,3-dimethylimidazolium)Cl (2.10 g, 15.83 mmol) in methylene chloride (25 mL) was mixed with a solution of $ZnBr_2$ (1.78 g, 7.90 mmol) in tetrahydrofuran (25 mL) and refluxed for 3 h. After cooling to room temperature, the white precipitate was collected by filtration. Yield: 93.9%; elemental analysis cald (%) for $C_{10}H_{18}Br_2Cl_2N_4Zn$: C 24.49, H 3.70, Br 32.59, Cl 14.46, N 11.43, Zn 13.33; found: C 24.23, H 3.75, Br 31.83, Cl 14.18, N 11.18, Zn 13.43; ^{1}H NMR(600 MHz, DMSO-d_6, 25 °C): $\delta = 3.84$(s, 6H, CH_3), 7.68(s, 2H, $C_3H_3N_2$), 9.06(s, 1H, $C_3H_3N_2$).

Other 1-alkyl-3-methylimidazolium zinc tetrahalides were similarly prepared.

2.3. Coupling reactions

All the coupling reactions were conducted in a 200-mL stainless-steel bomb reactor equipped with a magnet bar and an electrical heater. The reactor was charged with an appropriate catalyst and an epoxide and pressurized with CO_2 (≈ 1.4 MPa). The bomb was then heated to a specified reaction temperature with the addition of CO_2 from a reservoir tank to maintain a constant pressure. After the reaction, the bomb was cooled to room temperature, and the remaining epoxide was removed using an aspirator. The product mixture was analyzed by Hewlett Packard 6890 gas chromatography equipped with a flame-ionized detector and a DB-wax column (30 m × 0.32 mm × 0.25 µm), Hewlett Packard 6890-5973 MSD GC-mass spectrometry, and Young-Lin gel-permeation chromatography equipped with a refractive index detector.

3. Results and discussion

Bis(1-alkyl-3-methylimidazolium)zinc tetrahalides were prepared in high yields by reacting 1-alkyl-3-methylimidazolium with zinc halides as shown in Eq. (2).

It is interesting to note that the same (1-R-3-methylimidazolium)$_2$ZnX$_2$Y$_2$ can be obtained when X and Y are interchanged in the starting materials. For example, (1-butyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$, **3b** was obtained either from the reaction of $ZnCl_2$ and (1-butyl-3-methylimidazolium)Br or from the reaction of $ZnBr_2$ and (1-butyl-3-methylimidazolium)Cl.

The catalytic activities of various bis(1-R-3-methylimidazolium) zinc tetrahalides were evaluated for the coupling reactions of CO_2 and ethylene oxide (EO) or propylene oxide (PO) at 100 °C for 1 h. The molar ratios of epoxide to catalyst were set at 5000 for EO and 2000 for PO, respectively.

As shown in Table 1, ionic liquids such as 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium bromide exhibited extremely low activities, and zinc bromide was completely inactive (entries 1–3). However, the combination of zinc bromide with 1-butyl-3-methylimidazolium chloride or 1-butyl-3-methylimidazolium bromide exhibited a surprisingly high activity for the coupling reaction, giving TOF of 2112 for 1-butyl-3-methylimidazolium chloride–$ZnBr_2$ or 3545 for 1-butyl-3-methylimidazolium bromide–$ZnBr_2$ at 100 °C (entries 4 and 5). To our knowledge, these are the highest TOFs ever reported in the literature. Such high activities are most likely attributed to the in situ formation of new active complexes, bis(1-butyl-3-methylimidazolium) zinc tetrahalides from 1-butyl-3-methylimidazolium halide and $ZnBr_2$. This is supported by the fact that (1-butyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$ and (1-butyl-3-methylimidazolium)$_2$ZnBr$_4$ show similar activities to the corresponding catalytic systems of 1-butyl-3-methylimidazolium chloride–$ZnBr_2$ and 1-butyl-3-methylimidazolium bromide–$ZnBr_2$ (entries 9 and 10). By-products such as polyalkylene oxides and halogenated compounds were not detected by GC and GPC analysis.

The catalytic activities of imidazolium zinc tetrahalides were greatly influenced by the nature of halide ligands bonded to zinc atoms. The reactivity was found to be in the following order, $[ZnBr_4]^{2-} > [ZnBr_2Cl_2]^{2-} \gg [ZnCl_4]^{2-}$, suggesting the importance of the nucleophilicity of halide ligands.

The dissociation of a halide ion from the imidazolium zinc tetrahalide and the following attack of the halide ion on the carbon atom of an epoxide would take place more easily with more nucleophilic bromide ions. In contrast, the substitution on imidazolium cations was found to have a negligible effect on the catalytic activity.

As can be seen in Table 2, the effects of temperature and pressure were also investigated with complex **2b**. The TOF (h^{-1}) increased steeply with increasing temperature from 80 to 120 °C for both ethylene oxide and propylene oxide. On the contrary, the TOF (h^{-1}) remained almost constant when the pressure was changed from 2.1 to 4.8 MPa. Due to a possible explosion of ethylene oxide, the reaction was not performed at pressures lower than 2.1 MPa of CO_2.

To test the catalyst stability and reusability, the coupling reaction of ethylene oxide and CO_2 was performed with **2b**

Table 1
Catalytic activities of imidazolium zinc tetrahalide for the coupling reactions of CO_2 and epoxides[a]

Entry	Catalyst	TOF (h^{-1})[b]	
		EO	PO
1	(1-Butyl-3-methylimidazolium)Cl	10	5
2	(1-Butyl-3-methylimidazolium)Br	78	37
3	$ZnBr_2$	n.r.[c]	n.r.[c]
4	(1-Butyl-3-methylimidazolium)Cl + $ZnBr_2$	2112	1295
5	(1-Butyl-3-methylimidazolium)Br + $ZnBr_2$	3545	1679
6	(1,3-Dimethylimidazolium)$_2$ $ZnBr_2Cl_2$, **1b**	2697	1001
7	(1-Ethyl-3-methylimidazolium)$_2$ $ZnBr_2Cl_2$, **2b**	2137	1335
8	(1-Ethyl-3-methylimidazolium)$_2$ $ZnBr_4$, **2c**	3588	1617
9	(1-Butyl-3-methylimidazolium)$_2$ $ZnBr_2Cl_2$, **3b**	2538	1328
10	(1-Butyl-3-methylimidazolium)$_2$ $ZnBr_4$, **3c**	3579	1683
11	(1-Benzyl-3-methylimidazolium)$_2$ $ZnCl_4$, **4a**	210	79
12	(1-Benzyl-3-methylimidazolium)$_2$ $ZnBr_2Cl_2$, **4b**	2527	1201
13	(1-Benzyl-3-methylimidazolium)$_2$ $ZnBr_4$, **4c**	3424	1846

[a] Reactions were carried out at 100 °C and 3.5 MPa of CO_2 for 1 h. Molar ratios of epoxides to zinc were set at EO/Zn = 5000 and PO/Zn = 2000, respectively.

[b] TOF (h^{-1}): moles of alkylene carbonate/(moles of catalyst hour).

[c] No reaction.

Table 2
Effects of temperature and pressure of CO_2 for the coupling reactions of CO_2 and epoxides catalyzed by (1-ethyl-3-methylimidazolium)$_2$ $ZnBr_2Cl_2$, **2b**[a]

Entry	Temperature (°C)	Pressure of CO_2 (MPa)	TOF (h^{-1})[b]	
			EO	PO
1	140	3.4	4968	1985
2	120	3.4	4274	1962
3	100	3.4	2137	1335
4	80	3.4	841	169
5	100	4.8	2218	1320
6	100	3.4	2137	1335
7	100	2.8	2131	1328
8	100	2.1	2156	1291

[a] Reactions were carried out at various temperatures and pressures of CO_2 for 1 h. Molar ratios of epoxides to zinc were set at EO/Zn = 5000 and PO/Zn = 2000, respectively.

[b] TOF (h^{-1}): moles of alkylene carbonate/(moles of catalyst hour).

for 1 h at 100 °C and 3.4 MPa. After the reaction, ethylene carbonate and unreacted ethylene oxide were distilled off from the product mixture, and the remaining catalyst was reused for further reaction with a fresh charge of ethylene oxide and CO_2. As shown in Table 3, the catalyst retained most of its initial activity even after five runs, supporting the stability of imidazolium zinc tetrahalide catalysts.

Kisch and co-workers suggested the parallel requirement of both Lewis acid for the activation of alkylene oxide and Lewis base for the activation of CO_2 in the synthesis of cyclic carbonates from CO_2 and epoxides [9,10].

Likewise, in the case of imidazolium zinc tetrahalide-catalyzed coupling reactions, the zinc center in $[ZnX_2Y_2]^{2-}$ is expected to act as a Lewis acid for the coordination of an epoxide and the halide ion is expected to act as a Lewis base to ring open the coordinated epoxide.

Further experiments are in progress to fully characterize the active species and to elucidate the reaction mechanism.

Table 3
Catalyst recycling studies with (1-ethyl-3-methylimidazolium)$_2$ $ZnBr_2Cl_2$, **2b**[a]

Number of recycle	EC yield (%)[b]	TOF (h^{-1})[c]
1	43.3	2165
2	44.8	2238
3	43.8	2189
4	43.7	2187
5	44.4	2218

[a] Reactions were carried out at 100 °C and 3.5 MPa of CO_2 for 1 h. Molar ratio of EO to zinc was 5000.

[b] Isolated yield by distillation.

[c] TOF (h^{-1}): moles of alkylene carbonate/(moles of catalyst hour).

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