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Ionic liquid-derived zinc tetrahalide complexes: structure and application to the coupling reactions of alkylene oxides and CO_2

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Abstract

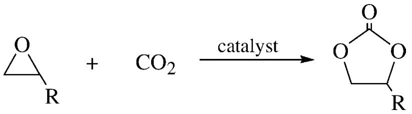
Various alkylene carbonates have been prepared in high yields by the coupling reactions of alkylene oxides with CO_2 in the presence of a dialkylimidazolium zinc tetrahalide complex, prepared from imidazolium halides and zinc halides. The single crystal X-ray diffraction analysis of an active species (1,3-dimethylimidazolium)$_2$$ZnBr_2Cl_2$ showed that two 1,3-dimethylimidazolium cations were paired with a dibromodichloro zincate dianion.

Keywords: Alkylene carbonate; Ionic liquid; Imidazolium; Zinc; Carbon dioxide

1. Introduction

The transformation of CO_2 into alkylene carbonates by the coupling reaction with epoxides has received much attention with regard to the utilization of CO_2, a gas responsible for global warming [1–4].

Alkylene carbonates are used as raw materials in a wide range of chemical reactions: the production of ethylene glycol esters, hydroxyalkyl derivatives, carbamates, alkylene sulfides, polyurethanes, polyesters and polycarbonates [5–7]. Recently, there is an increasing demand for cyclic carbonates as solvent for polymer and gel electrolytes in secondary and fuel-cell batteries [8,9].



Accordingly, a substantial literature on the catalyst development and mechanism for the coupling reactions has been reported [10–12]. The use of transition metal halide catalysts along with *t*-alkyl ammonium halide or alkali metal halide has been shown to be a highly active combination for promoting the coupling reactions, where the halide ligands act as nucleophiles [13–16]. The catalytic systems composed of transition metal halide ($AlCl_3$, $NiCl_2$, $MoCl_5$, etc.) and Lewis base such as amines or phosphines have been employed in the selective formation of cyclic carbonates [17]. Zinc(II) complexes have also been used as catalysts, owing to their high activity in the cyclization and copolymerization of CO_2 and epoxides [18–21].

Recently, imidazolium-based ionic liquids have been employed as reaction media and/or catalysts for the coupling reactions but the productivity were not high enough for the practical purposes even at elevated temperatures [22].

During the course of our studies on the development of active catalysts for the coupling reaction, we have found that the catalytic activities of imidazolium-based ionic liquids can be drastically enhanced by the co-presence of zinc halides due to the formation of highly active species, imidazolium zinc tetrahalides [23].

Herein, we report the synthesis, characterization and reactivities of a series of imidazolium zinc tetrahalide complexes of the general formula (1-R-3-methylimidazolium)$_2$-ZnX_aY_{4-a} (R: CH_3, C_2H_5, n-C_4H_9, $CH_2C_6H_5$; X, Y: Cl, Br; a: 0, 2, 4) for the coupling reactions of various alkylene oxide with CO_2 as well as the single crystal X-ray diffraction analysis of (1,3-dimethylimidazolium)$_2$$ZnCl_2Br_2$.

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2. Methods

All manipulations were carried out under an argon atmosphere unless otherwise stated. Solvents were freshly distilled prior to use according to the literature procedures. Ethylene oxide (EO) was purchased from Honam Petrochemical Co. and used as received. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification. CO_2 was purchased from Sin Yang gas. The 1-R-3-methylimidazolium halides were prepared according to the literature procedure [24–26].

2.1. Synthesis of (1,3-dimethylimidazolium)$_2$ZnBr$_2$Cl$_2$ ([Dmim]$_2$ZnBr$_2$Cl$_2$)

A solution of (1,3-dimethylimidazolium)Cl, [Dmim]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 tetrahydrofurane (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, $C_3H_3N_2$).

The same compound was also obtained from the reaction of [Dmim]Cl and $ZnBr_2$. Other 1-alkyl-3-methylimidazolium zinc tetrahalides were similarly prepared.

2.2. (1-Ethyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$ ([Emim]$_2$ZnBr$_2$Cl$_2$)

Yield: 89.7%; elemental analysis cald. (%) for $C_{12}H_{22}Br_2Cl_2N_4Zn$: C 27.80, H 4.28, Br 30.83, Cl 13.68, N 10.81, Zn 12.61; found: C 27.55, H 4.31, Br 30.95, Cl 13.53, N 10.75, Zn 12.58; ^{1}H NMR (600 MHz, DMSO-d$_6$, 25 °C): $\delta = 1.41$ (t, 3H, CH_2CH_3), 3.82 (s, 3H, CH_3), 4.18 (q, 2H, CH_2CH_3), 7.64 (s, 1H, $C_3H_3N_2$), 7.79 (s, 1H, $C_3H_3N_2$), 9.15 (s, 1H, $C_3H_3N_2$).

2.3. Synthesis of (1-butyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$ ([Bmim]$_2$ZnBr$_2$Cl$_2$)

Yield: 98.6%; elemental analysis cald. (%) for $C_{16}H_{30}Br_2Cl_2N_4Zn$: C 33.45, H 5.26, Br 27.81, Cl 12.34, N 9.75, Zn 11.38; found: C 33.29, H 5.38, Br 27.35, Cl 12.19, N 9.62, Zn 11.27.

2.4. Synthesis of (1-benzyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$ ([Bzmim]$_2$ZnBr$_2$Cl$_2$)

Yield: 85.8%; elemental analysis cald. (%) for $C_{22}H_{26}Br_2Cl_2N_4Zn$: C 41.12, H 4.08, Br 24.87, Cl 11.03, N 8.72, Zn 10.18; found: C 41.38, H 4.21, Br 24.58, Cl 11.00, N 8.59, Zn 10.03; ^{1}H NMR (600 MHz, DMSO-d$_6$, 25 °C): $\delta = 3.84$ (s, 3H, CH_3), 5.42 (s, 2H, $CH_2C_6H_5$), 7.40 (m, 5H, C_6H_5), 7.71 (s, 1H, $C_3H_3N_2$), 7.80 (s, 1H, $C_3H_3N_2$), 9.21 (s, 1H, $C_3H_3N_2$).

2.5. Synthesis of (1-ethyl-3-methylimidazolium)$_2$ZnBr$_4$ ([Emim]$_2$ZnBr$_4$)

Yield: 92.3%; elemental analysis cald. (%) for $C_{12}H_{22}Br_4N_4Zn$: C 23.73, H 3.65, Br 52.63, N 9.23, Zn 10.77; found: C 23.58, H 3.72, Br 52.75, N 9.18, Zn 10.65; ^{1}H NMR (600 MHz, DMSO-d$_6$, 25 °C): $\delta = 1.40$ (t, 3H, CH_2CH_3), 3.83 (s, 3H, CH_3), 4.20 (q, 2H, CH_2CH_3), 7.61 (s, 1H, $C_3H_3N_2$), 7.78 (s, 1H, $C_3H_3N_2$), 9.21 (s, 1H, $C_3H_3N_2$).

2.6. Coupling reactions of epoxides and CO$_2$

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 down to room temperature. The product mixture was analyzed by Hewlett Packard 6890 gas chromatography (GC) equipped with a flame ionized detector and a DB-wax column (30 m × 0.32 mm × 0.25 μm), and Hewlett Packard 6890–5973 MSD GC–mass spectrometry.

3. Results and discussion

An active species was isolated as a white powder from the coupling reaction of CO_2 and ethylene oxide performed at 100 °C, 500 psig of CO_2 and EO/Zn = 100 in the presence of a catalytic system composed of 1,3-dimethylimidazolium bromide ([Dmim]Br) and zinc chloride.

The ^{1}H NMR spectroscopic and elemental analysis data showed that the powder is a zinc halide complex containing two imidazolium moieties. The ambiguous spectroscopic and elemental analysis data led us to carry out single crystal X-ray diffraction study, which revealed that the white powder was [Dmim]$_2$ZnCl$_2$Br$_2$. The crystals of [Dmim]$_2$ZnCl$_2$Br$_2$ were grown in a DMSO/toluene solvent mixture at room temperature. An ORTEP of its molecular structure is shown in Fig. 1, where selected bond distances and angles are also provided.

The crystal of [Dmim]$_2$ZnCl$_2$Br$_2$ contains two independent molecules in the asymmetric-crystal unit. Each zinc center is surrounded by four halide ligands and possesses a distorted tetrahedral ligand environment. Unfortunately, the exact position of bromide and chloride in tetrahedral zinc center could not be determined due to a disorder in the crystal system. Interestingly, two imidazolium cations were paired with a tetrahalo zincate dianion ($[ZnBr_2Cl_2]^{2-}$) in the solid state.

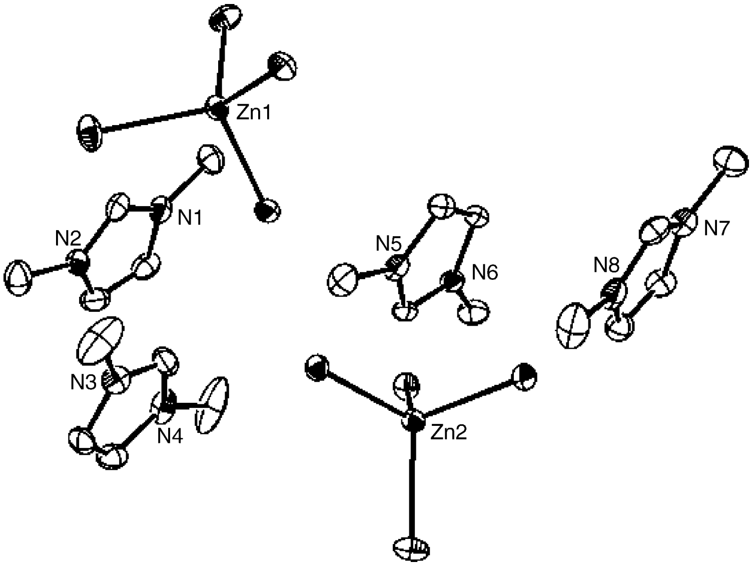

Fig. 1. Molecular structures of [Dmim]$_2$ZnCl$_2$Br$_2$. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–Cl(Br)(1) = 2.2988 (15), Zn(1)–Cl(Br)(2) = 2.3364 (12), Zn(1)–Cl(Br)(3) = 2.3881 (15), Zn(1)–Cl(Br)(4) = 2.3926 (15), Zn(2)–Cl(Br)(5) = 2.3416 (13), Zn(2)–Cl(Br)(6) = 2.3505 (15), Zn(2)–Cl(Br)(7) = 2.3622 (14), Zn(2)–Cl(Br)(8) = 2.3293 (14), Cl(Br)(1)–Zn(1)–Cl(Br)(2) = 111.06 (6), Cl(Br)(1)–Zn(1)–Cl(Br)(3) = 107.44 (5), Cl(Br)(1)–Zn(1)–Cl(Br)(4) = 107.61 (5), Cl(Br)(2)–Zn(1)–Cl(Br)(3) = 108.91 (5), Cl(Br)(2)–Zn(1)–Cl(Br)(4) = 111.75 (5), Cl(Br)(3)–Zn(1)–Cl(Br)(4) = 109.98 (6), Cl(Br)(5)–Zn(2)–Cl(Br)(6) = 109.35 (5), Cl(Br)(5)–Zn(2)–Cl(Br)(7) = 111.64 (5), Cl(Br)(5)–Zn(2)–Cl(Br)(8) = 110.75 (5), Cl(Br)(6)–Zn(2)–Cl(Br)(7) = 107.93 (6), Cl(Br)(6)–Zn(2)–Cl(Br)(8) = 107.04 (5), Cl(Br)(7)–Zn(2)–Cl(Br)(8) = 109.98 (5).

In order to confirm that [Dmim]$_2$ZnCl$_2$Br$_2$ is a real-active species for the coupling reaction performed in the presence of [Dmim]Br and ZnCl$_2$, the activity of [Dmim]$_2$ZnCl$_2$Br$_2$ was compared with that of the catalytic system composed of [Dmim]Br and ZnCl$_2$for the coupling reaction of CO$_2$ and ethylene oxide at 100 °C and 500 psig with a molar ratio of EO/Zn = 500.

As can be seen in Table 1, [Dmim]$_2$ZnCl$_2$Br$_2$ was found to exhibit the similar activity to the catalytic system consisting of [Dmim]Br and ZnCl$_2$. The active species, [Dmim]$_2$ZnCl$_2$Br$_2$ was obtained in high yield over 90% either by reacting [Dmim]Br with ZnCl$_2$ or from the reaction of [Dmim]Cl and ZnBr$_2$, suggesting that bromide and chloride anions in [Dmim]$_2$ZnCl$_2$Br$_2$ can be exchanged. Other imidazolium zinc complexes were similarly prepared.

The catalytic activity of [Dmim]$_2$ZnCl$_2$Br$_2$ was evaluated for the coupling reactions of CO$_2$ and various alkylene oxide to produce corresponding alkylene carbonates, and the results are listed in Table 2. Most of the alkylene oxides tested were readily converted to the corresponding alkylene oxides but the reactivity of alkylene oxide was greatly affected by the substituent at the carbon atom of the epoxide. Ethylene oxide and alkylene oxides with less bulkier substituents, produced corresponding alkylene oxides in high yields. However, alkylene oxides with bulky substituents around epoxide groups gave much lower yields of alkylene carbonates. This can be clearly seen by comparing the reactivities of 1,2-epoxybutane, glycidylisopropyl ether and *t*-butylglycidyl ether. The most crowded *t*-butylglycidyl ether showed the lowest reactivity while the least crowded 1,2-epoxybytane exhibited the highest reactivity. The steric crowdness around epoxide group is likely to prevent the coordination of alkylene oxide to zinc center. The lower reactivities of epicholorohydrin and hexafluoropropylene

Table 1
Coupling reactions of CO$_2$ and ethylene oxide in the presences various catalysts or catalytic systems[a]

Entry	Substrate	Yield (%)	TOF (h^{-1})[b]
1	[Dmim]Cl	9	45
2	[Dmim]Br	11	55
3	ZnCl$_2$	n.r.[c]	n.a.
4	ZnBr$_2$	n.r.[c]	n.a.
5	[Dmim]Cl/ZnBr$_2$	90	450
6	[Dmim]Br/ZnCl$_2$	92	460
7	[Dmim]$_2$ZnBr$_2$Cl$_2$	98	490

[a] Reactions were carried out at 100 °C and 500 psig of CO$_2$ for 1 h. Molar ratio of ethylene oxide to zinc was set at 500.

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

Table 2
Catalytic activities of [Dmim]$_2$ZnBr$_2$Cl$_2$ for the coupling reactions of CO$_2$ and various alkylene oxides[a]

Entry	Substrate	Yield (%)	TOF (h^{-1})[b]
1	Propylene oxide	100	500
2	1,2-Epoxybutane	98	490
3	Glycidylisopropyl ether	23	115
4	*t*-Butylglycidyl ether	11	55
5	Epichlorohydrin	77	385
6	Styrene oxide	77	385
7	Hexafluoropropylene oxide	1	5

[a] Reactions were carried out at 100 °C and 500 psig of CO$_2$ for 1 h. Molar ratio of epoxide to zinc was set at 500.

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

Table 3
Catalytic activities of various imidazolium zinc tetrahalides[a]

Entry	Catalyst[b]	Substrate	TOF (h^{-1})[c]
1	$[Dmim]_2ZnBr_2Cl_2$	Propylene oxide	500
2	$[Emim]_2ZnBr_2Cl_2$	Epichlorohydrin	410
3	$[Bmim]_2ZnBr_2Cl_2$	1,2-Epoxybutane	485
4	$[Bzmim]_2ZnBr_2Cl_2$	Styrene oxide	390
5	$[Emim]_2ZnBr_4$	Epichlorohydrin	500
6	$[Emim]_2ZnCl_4$	Epichlorohydrin	30

[a] Reactions were carried out at 100 °C and 500 psig of CO_2 for 1 h. Molar ratio of epoxide to zinc was set at 500.

[b] Emim: 1-ethyl-3-methylimidazolium; Bmim: 1-butyl-3-methylimidazolium; Bzmim: 1-benzyl-3-methylimidazolium.

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

oxide in comparison with propylene oxide can be largely attributed to the electron-withdrawing effects of chlorine and fluorine atoms. The presence of highly electronegative substituent reduces the electron density on the oxygen atom of epoxide, and therefore the ability of epoxide to coordinate to zinc center become reduced, which is presumed to be the first step in the coupling reaction. The reason for the relatively lower reactivity of styrene oxide seems to be a combination of steric and electronic effect of phenyl group.

Various imidazolium zinc tetrahalide complexes were tested for their activities in the coupling reactions of CO_2 and alkylene oxides (Table 3). The activities of imidazolium zinc tetrahalides were not significantly affected by the variation of imidazolium cations. On the other hand, the activities were greatly influenced by halide groups bonded to zinc center. From these results, it is likely that the imidazolium cation only plays a role in stabilizing an active zinc tetrahalide dianion and not in controlling the activity.

The dissociation of a halide ion from the zinc tetrahalide dianion and the following attack of the halide ion on the carbon atom of the epoxide would take place more easily with more nucleophilic bromide ion, giving the following activity order: $[ZnBr_4]^{2-} > [ZnBr_2Cl_2]^{2-} \gg [ZnCl_4]^{2-}$.

4. Conclusions

A series of ionic liquid-based imidazolium zinc tetrahalide and $(\text{1-R-3-methylimidazolium})_2ZnX_2Y_2$, were prepared by reacting ZnX_2 with (1-R-3-methylimidazolium)Y.

The single crystal X-ray structural analysis and elemental analysis of $(\text{1,3-dimethylimidazolium})_2ZnBr_2Cl_2$ revealed that two imidazolium cations were paired with a dibromodichloro zincate dianion.

The catalytic activities of imidazolium zinc tetrahalide were evaluated for the coupling reactions of epoxides and CO_2, and the effects of halide ions, imidazolium cations, temperature and pressure were investigated. The catalytic activity of $(\text{1-R-3-methylimidazolium})_2ZnX_2Y_2$ was found to increase with increasing nucleophilicity of halide ion. But, the substitution on the imidazolium cation showed a negligible effect on the catalytic activity. The formation of cyclic carbonate was strongly dependent on the temperature but independent of the pressure of CO_2. The reactivity of alkylene oxide was greatly affected by the substituent at the carbon atom of the epoxide. Ethylene oxide and alkylene oxides with less bulkier substituents produced corresponding alkylene oxides in high yields. However, alkylene oxides with bulky or electron-withdrawing substituents around epoxide groups gave much lower yields of alkylene carbonates.

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