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Zn-containing ionic liquids bearing dialkylphosphate ligands for the coupling reactions of epoxides and CO_2

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ABSTRACT

Zn-containing room temperature ionic liquids (Zn-RTILs), prepared from the reactions of $ZnBr_2$ with 1-alkyl-3-methylimidazolium dialkyphosphates ([RMIm][R_2PO_4]), were highly active for the coupling reactions of CO_2 with epoxides, producing corresponding cyclic carbonates in high yields. FAB-mass spectral and computational results suggest that $[ZnBr(R_2PO_4)_2]^-$ could be an active species for the coupling reaction. Decomposition of cyclic carbonates into epoxides and CO_2 during the product recovery process via vacuum distillation was almost negligible even in the presence of a Zn-RTIL up to 130 °C.

1. Introduction

The transformation of CO_2 into 5-membered cyclic carbonates through the coupling reaction with epoxides is one of the most effective ways to utilize CO_2, a green house gas [1,2]. Cyclic carbonates are valuable chemicals that are being widely used as electrolyte components of lithium ion batteries, monomers of polycarbonates, aprotic polar solvents, paint strippers, adhesives, cosmetics, and reactants for many chemical reactions [3–6]. Since the first commercialization of cyclic carbonates from the coupling reactions using KI in 1950s, tremendous effort has been devoted to search for active catalysts to meet the increasing demand of cyclic carbonates. As a result, a large number of catalysts and catalytic systems have been developed, including phosphonium iodide, transition metal complexes, supported metal complexes, electroreduction, and ionic liquids (ILs) [7–17]. It has also been reported that ILs bearing a zinc tetrahalide anion, prepared from the reaction of zinc halides and an ILs with a halide anion, exhibit surprisingly high activities toward the coupling reactions [18–20]. The improvement of the catalytic activity has been significant with the discovery of the afore-mentioned Zn-containing ILs. However, the practical application of these catalysts has been restricted because cyclic carbonates are found to decompose into epoxide and CO_2 in the presence of an IL bearing a zinc tetrahalide anion during the product recovery process via vacuum distillation at elevated temperature [21,22]. Catalyst decomposition is another problem encountered in the synthesis of cyclic carbonates, which inevitably produces unwanted side products [23]. To circumvent these problems, it is desirable to develop new types of active and stable catalysts that are highly active for the coupling reaction of epoxides and CO_2, but almost inert to the decomposition reactions of cyclic carbonates. The catalyst for the coupling reaction is also capable of catalyzing the decomposition of cyclic carbonates into epoxides and CO_2, especially at elevated temperatures in the absence of CO_2 pressure. For this reason, a considerable loss of cyclic carbonates is often observed during the recovery of a cyclic carbonate from a catalyst-containing reaction mixture through vacuum distillation process.

For the decomposition to take place, there should exist a substantial interaction between the cyclic carbonate and the catalyst. Therefore, to prevent the decomposition, the catalyst should be designed in a way to minimize the interaction with cyclic carbonate. As an approach to reach this goal, we have attempted to use imidazolium-based zinc containing ILs bearing dialkylphosphate ligands as catalysts for the coupling reactions of epoxide with CO_2.

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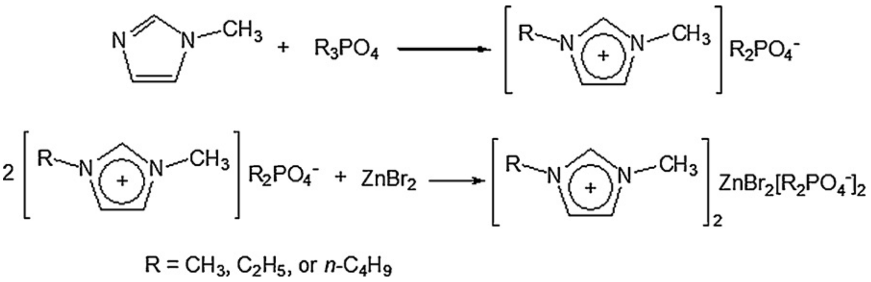


Scheme 1. Synthesis of Zn-RTILs.

It is hoped that the presence of bulky and chelating dialkylphosphate ligands on the zinc atom could play a role in limiting the interaction between the catalyst and cyclic carbonate as well as in enhancing the catalyst stability.

In this paper, we report the synthesis of Zn-containing room temperature ionic liquids (Zn-RTILs) from the reaction of $ZnBr_2$ with 1-alkyl-3-methylimidazolium dialkylphosphate ([RMIm][R_2PO_4]; R = C_1–C_4 alkyl) as illustrated in Scheme 1 and their catalytic activities for the coupling reactions of CO_2 with epoxides (see Scheme 2). The catalytic roles of Zn-RTILs for the coupling reactions and for the decomposition of ethylene carbonate (EC) have also been discussed in detail on the basis of experimental, spectroscopic, and computational calculations.

2. Experimental

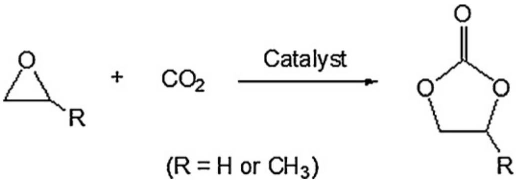
2.1. General

Propylene oxide (PO) and all other chemicals to prepare Zn-RTILs were purchased from Aldrich Chemical Co. and were used without further purification, unless otherwise stated. Solvents were freshly distilled before use according to the literature procedures [24]. Ethylene oxide (EO) and CO_2 were obtained from Honam Petrochemical Co. and Sin Yang Gas Co., respectively, and used as received. [RMIm][R_2PO_4] were prepared according to the literature procedure by reacting 1-methylimidazole with corresponding trialkylphosphates [25,26].

^{1}H spectra were recorded on a Varian Unity 400 spectrometer. Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrophotometer (Thermo Electron Co.). To avoid contact with water and air, FT-IR measurements were performed using a specially designed IR cell equipped with two KRS-5 windows (see the Supplementary data).

2.2. Synthesis of Zn-RTILs

Zn-RTILs were prepared by reacting anhydrous $ZnBr_2$ with [RMIm][R_2PO_4] at 100 °C. In a typical experiment, $ZnBr_2$ (2.25 g, 10 mmol) was reacted with [EMIm][Et_2PO_4] (5.29 g, 20 mmol) at 100 °C for 1 h to afford bis(1-ethyl-3-methylimidazolium) dibromobis(dimethylphosphato)zinc ([EMIm]$_2$[$Br_2Zn(Et_2PO_4)_2$]) as a transparent viscous liquid.



Scheme 2. Coupling reaction of CO_2 with epoxide.

Other Zn-RTILs were prepared in an analogous manner to that employed for the synthesis of [EMIm]$_2$[$Br_2Zn(Et_2PO_4)_2$].

2.3. FAB-mass spectral analysis of Zn-RTILs

FAB-mass spectra for the characterization of Zn-containing ILs were recorded with a JMS-700 Mstation double focusing mass spectrometer (JEOL, Tokyo, Japan) using a MS-MP9020D data system. The ion source was operated at 10 kV accelerating voltage with a mass resolution of 1500 (10% valley). Fast atoms were produced by FAB using a xenon atom gun operated at 6 keV. Samples were dissolved in methanol and mixed with 1 μL of 3-nitrobenzyl alcohol (NBA, Sigma, St. Louis, MO, USA) on a FAB probe tip.

2.4. Coupling reactions

All the coupling reactions were conducted in a 100 mL stainless-steel bomb reactor equipped with a magnet bar and an electrical heater. The reactor was loaded with an appropriate Zn-RTIL and an epoxide, and pressurized with CO_2 (1.5 MPa). The reactor was then heated to a specified reaction temperature and the pressure was maintained constant at 3.4 MPa by means of a CO_2 reservoir cylinder equipped with a high pressure regulator. After the completion of the reaction, volatiles were removed using an aspirator and the remaining product mixture was analyzed by a Hewlett Packard 6890 gas chromatograph equipped with a flame ionized detector and a DB-wax column (30 m × 0.32 mm × 0.25 μm), and a Hewlett Packard 6890-5973 MSD GC–mass spectrometer. For GC and GC–mass analysis, product mixture (1 g) was dissolved in methylene chloride (5 mL) and passed through a short silica gel or alumina column to remove small amounts of Zn-RTIL catalyst.

2.5. Quantum mechanical calculations

The formations of dibromodimethylphosphatozinc ([$Br_2Zn(Me_2PO_4)$]$^-$, [**Zn–P$_1$**]$^-$) and 1,3-dimethylimidazolium dibromobis(dimethylphosphato)zinc ([DMIm][$Br_2Zn(Me_2PO_4)_2$]$^-$, [**Zn–P$_2$**]$^-$) from $ZnBr_2$ and [DMIm][Me_2PO_4], and the coupling reaction of EO and CO_2 in the presence of [**Zn–P$_2$**]$^-$ were theoretically investigated using a Gaussian 03 program [27]. The geometry optimizations and thermodynamic corrections were performed with hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange-correlation functional with the 6–31 + G* basis sets for C, H, N, O, and LanL2DZ(ECP) for Zn, P, and Br. In order to obtain the most stable geometries, all kinds of possible interaction patterns were optimized. No restrictions on symmetries were imposed on the initial structures. All stationary points were verified as minima by full calculation of the Hessian and a harmonic frequency analysis. For comparison, calculation on the formations of neutral Zn-RTILs, 1-3-dimethylimidazolium dibromodimethylphosphatozinc ([DMIm][$Br_2Zn(Me_2PO_4)$], **Zn–L**) and bis(1,3-dimethylimidazoloim) dibromobis(dimethylphosphato)zinc ([DMIm]$_2$[$Br_2Zn(Me_2PO_4)_2$], **Zn–2L**) were also conducted.