



Ionic-liquid-catalyzed decarboxylation of glycerol carbonate to glycidol

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ABSTRACT

Decarboxylation of glycerol carbonate (GLC) to produce 2,3-epoxy-1-propanol (glycidol) was conducted using various kinds of ionic liquids (ILs) as catalysts. ILs bearing an anion with medium hydrogen-bond basicity such as NO_3^- and I^- exhibited the higher glycidol yields than those having an anion with low or strong hydrogen-bond. FT-IR spectroscopic analysis shows that both GLC and glycidol interact with anions of ILs through their hydroxyl groups. It was possible to improve the yield of glycidol when a zinc salt with a medium Lewis acidity was co-present along with an IL. The yield of glycidol was greatly increased up to 98% when the decarboxylation was conducted in the presence of a high-boiling aprotic solvent. Computational calculations on the mechanism using 1-butyl-3-methylimidazolium nitrate as a catalyst revealed that the first step is the NO_3^- -assisted ring-opening of GLC followed by the ring closure, resulting in the formation of a 3-membered ring intermediate species.

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1. Introduction

The use of glycerol, produced in large quantities as a co-product of biodiesels, as a renewable feedstock for synthesizing various value-added chemicals and clean fuels has been attracting recent interest because the fate of the biodiesel industry is heavily dependent on the development of suitable applications of glycerol [1–3]. Accordingly, tremendous effort has been devoted to convert glycerol into valuable chemicals, including 1,3-propanediol, epichlorohydrin, acrolein, glyceric acid, dihydroxy acetone, etc., but only few of those chemicals has been commercialized yet, possibly due to the failure in finding active and selective catalysts. Recently, focus has also been turned to the synthesis of glycerol carbonate (GLC) from glycerol because GLC has many potential applications as a high-boiling polar solvent, an intermediate of polyurethanes, glycidol, etc. [4,5].

Of various applications of GLC, we are particularly interested in the synthesis of glycidol because glycidol possesses favorable properties making it suitable for use in stabilizers, plastics modifiers, surfactants, and fire retardants. Thus, glycidol can be used in a wide variety of industrial fields including the textile, plastic, pharmaceutical, cosmetic, and photochemical industries [6,7].

Glycidol is produced industrially through the oxidation of allyl alcohol using hydrogen peroxide as the oxidant in the presence of tungsten oxide-based catalyst or through the reaction of epichlorohydrin with bases [8,9]. However, those conventional processes to manufacture glycidol suffer from several drawbacks such as the high cost of raw materials and/or the generation of waste by-products. In this context, the synthesis of glycidol from the direct decarboxylation of GLC, as shown in Scheme 1, is worthy of attention in terms of economic and environmental points of view [10,11]. However, unfortunately, only very little information has been disclosed on the synthesis of glycidol from GLC.

In previous papers, we have shown that the ionic-liquid (IL)-based catalysts used for the synthesis of alkylene carbonates from the carboxylation of epoxides are also capable of catalyzing the decarboxylation of alkylene carbonates in the absence of CO_2 [12,13]. With this in mind, we have attempted to use ILs as catalysts for the decarboxylation of GLC to produce glycidol.

Herein, we report that ILs can also be used as efficient catalysts for the decarboxylation of GLC and that the catalytic activity of an IL is closely related to the hydrogen-bond basicity of the anion of the ILs.

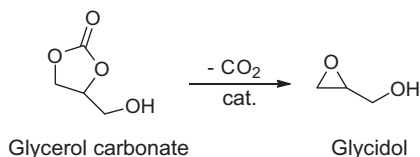
2. Experimental

2.1. General

All of the chemicals used for the synthesis of ILs and glycidol were purchased from Aldrich Chemical Co. (USA) and used as

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Scheme 1. Decarboxylation of glycerol carbonate (GLC) to glycidol.

received without further purifications. GLC was obtained from TCI (Japan) and ILS including 1-butyl-3-methylimidazolium nitrate ([BMIm]NO₃), 1-butyl-2,3-dimethylimidazolium nitrate, and 1-butyl-3-methylimidazolium bicarbonate ([BMIm]HCO₃) were prepared according to the literature procedure [14,15]. Other ILS tested for the decarboxylation of GLC were purchased from C-Tri Co. (Korea).

The interactions of ILS with GLC or glycidol were investigated using a FT-IR (iS10, Nicolet) spectrometer equipped with a Smart Omni-Transmission accessory.

2.2. Decarboxylation of GLC

In a 100 mL three-necked flask equipped with a condenser and an electrical heater, GLC was decarboxylated into glycidol in the presence of a catalyst and/or a solvent at a specified temperature under a reduced pressure of 2.67 kPa. Volatiles produced during the decarboxylation reaction were collected in a cold receiver immersed in a dry ice–acetonitrile bath. After the completion of the reaction, the product mixture in the flask were analyzed using a HPLC (Waters) equipped with an Aminex HPX-87H column (Bio-rad) and a RI detector (Waters 410). The mobile phase used was a 5 mM H₂SO₄ aqueous solution, and the flow rate was set at 0.6 mL/min. The volatiles collected in the cold receiver were analyzed by a gas chromatograph (Agilent, 6890N) equipped with a HP-INNOWAX capillary column (30 m × 0.32 mm × 0.25 μm) and a flame-ionization detector, and a GC–Mass spectrometer (Hewlett Packard 6890–Agilent 5973 MSD).

2.3. Computational calculations

The mechanism for the IL-assisted decarboxylation of GLC leading to glycidol was theoretically investigated using a Gaussian 09 program [16]. The geometry optimizations and thermodynamic corrections were performed using the hybrid Becke 3–Lee–Yang–Parr (B3LYP) exchange–correlation functional with the 6–31+G* basis sets for C, H, N, and O. For simplicity, [EMIm]NO₃ (1-butyl-3-methylimidazolium nitrate) was used instead of [BMIm]NO₃ and the bulk solvent effect was not included in the calculation. In order to obtain the most stable geometries, all possible interaction patterns were optimized. Restrictions on symmetries were not imposed on the initial structures. All stationary points were verified as minima through full calculation of the Hessian and a harmonic frequency analysis.

3. Results and discussion

3.1. Activities of alkali metal salts: effect of anion

As the first step for the development of high-performance catalysts for the decarboxylation of GLC, we have undertaken a comprehensive investigation of the activities of various sodium salts because some sodium salts like NaCl and Na₂SO₄ are known to catalyze the decarboxylation of GLC [11,17].

Decarboxylation of GLC was conducted in the presence of an alkali metal salt at 175 °C for 45 min under a reduced pressure of

Table 1
Activities of various alkali metal salts for the decarboxylation of GLC.^a

Entry	Catalyst	C (%)	Y (%)	S (%)	TOF (h ⁻¹)
1	None	4.5	3.4	73.9	–
2	Na ₂ SO ₄	72.2	55.9	77.4	149
3	NaF	100	38.7	38.7	103
4	NaCl	97.5	62.0	63.6	165
5	NaBr	80.6	53.7	66.6	143
6	NaNO ₃	94.7	67.0	70.7	179
7	NaN(CN) ₂	100	45.5	45.5	121
8	NaCH ₃ CO ₂	100	33.7	33.7	90
9	NaNO ₂	100	40.8	40.8	109
10	Na ₂ SO ₃	99.2	56.4	56.9	150
11	NaPF ₆	4.7	1.2	26.1	3
12	NaBF ₄	6.3	2.0	31.5	5

TOF (h⁻¹) = moles of glycidol produced/moles of catalyst/h.

^a Reaction conditions: GLC = 169 mmol, molar ratio of catalyst/GLC = 0.005, T = 175 °C, P = 2.67 kPa, t = 45 min. C = GLC conversion, Y = glycidol yield, S = glycidol selectivity.

2.67 kPa. As can be seen in Table 1, the decarboxylation of GLC proceeded extremely slowly in the absence of a catalyst, resulting in a conversion as low as 4.5%. Interestingly, the conversion was almost quantitative when 0.5 mol% of NaCl with respect to GLC was used as a catalyst, but the yield and selectivity of glycidol were only 62.0% and 63.6%, respectively, due to the formation of dimeric side products of glycidol, including 1,4-dioxane-2,5-dimethanol, 3-(oxirane-2-yl)oxypropane-1,2-diol, and 1,4-dioxane-2,6-dimethanol (see Scheme S1 in the Supporting information).

Of the sodium salts tested, only NaNO₃ showed higher glycidol yield than that of NaCl. All the other sodium salts exhibited catalytic performances lower than that of NaCl in terms of either conversion or yield. It is worthwhile to note that the catalytic activities of NaPF₆ and NaBF₄ are almost negligible, strongly indicating that anions play pivotal roles in the decarboxylation of GLC.

3.2. Effect of cation

As NaCl exhibited higher performance than most of the other sodium salts, it was hoped that the alkali metal chlorides, CsCl and RbCl, which have larger-sized cations than that of Na⁺, would give better performance due to the longer cation–anion distance and consequently due to the increased nucleophilicity or basicity of Cl⁻ in these alkali metal chlorides. However, as shown in Table 2, there was observed no distinct correlation between the catalytic activity and the size of the alkali metal cation. In contrast, metal chlorides with a multivalent cation such as MgCl₂, ZnCl₂, and AlCl₃ exhibited almost no activity for the decarboxylation, implying that

Table 2
Effect of cation for the decarboxylation of GLC.^a

Entry	Catalyst	C (%)	Y (%)	S (%)	TOF (h ⁻¹)
1	NaCl	97.5	62.0	63.6	165
2	LiCl	98.8	61.2	61.9	163
3	KCl	92.6	59.7	64.5	159
4	RbCl	99.6	54.7	54.7	146
5	CsCl	99.9	62.4	62.4	166
6	[BMIm]Cl	99.8	57.1	57.3	152
7	MgCl ₂	4.9	2.5	51.0	7
8	AlCl ₃	2.4	2.1	77.8	6
9	SnCl ₄	13.4	1.5	11.3	4
10	ZnCl ₂	3.5	2.0	57.1	5
11	FeCl ₃	5.2	1.8	34.6	5

^a Reaction conditions: GLC = 169 mmol, molar ratio of catalyst/GLC = 0.005, T = 175 °C, P = 2.67 kPa, t = 45 min. C = GLC conversion, Y = glycidol yield, S = glycidol selectivity, TOF (h⁻¹) = moles of glycidol produced/moles of catalyst/h.

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