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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.

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-propandiol, epichlorohydrine, 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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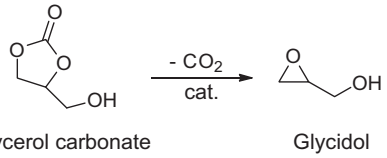


Scheme 1. Decarboxylation of glycerol carbonate (GLC) to glycidol.

received without further purifications. GLC was obtained from TCI (Japan) and ILs including 1-butyl-3-methylimidazolium nitrate ([BMIm]NO_3), 1-butyl-2,3-dimethylimidazolium nitrate, and 1-butyl-3-methylimidazolium bicarbonate ([BMIm]HCO_3) 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 (Biorad) and a RI detector (Waters 410). The mobile phase used was a 5 mM H_2SO_4 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]NO_3 (1-butyl-3-methylimidazolium nitrate) was used instead of [BMIm]NO_3 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 Na_2SO_4 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 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-(oxrian-2-yloxy)propane-1,2-diol, and 1,4-dioxane-2,6-dimethanol (see Scheme S1 in the Supporting information).

Of the sodium salts tested, only $NaNO_3$ 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 $NaPF_6$ and $NaBF_4$ are almost negligible, strongly indicating that anions play pivotal roles in the decarboxylation of GLC.

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_2SO_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	$NaCH_3CO_2$	100	33.7	33.7	90
9	$NaNO_2$	100	40.8	40.8	109
10	Na_2SO_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.

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 $MgCl_2$, $ZnCl_2$, and $AlCl_3$ 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	FeCl3	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.

the Lewis acidity of cations is also an important factor in determining the catalytic activity of metal halides. From these results, it is cautiously concluded that both the Lewis acidity of the cation and the nucleophilicity of the anion should be considered together for a metal salt catalyst to be active and selective for the decarboxylation of GLC. However, as can be seen in Tables 1 and 2, none of the metal catalysts tested were very selective toward the formation of glycidol.

3.3. Ionic-liquid-catalyzed decarboxylation

As a means of improving the selectivity and yield of glycidol, we have attempted to use ILs because the acidity of the cation and the nucleophilicity of the anion can be tailored, and some ILs bearing a halide anion are known to catalyze the decomposition of ethylene carbonate into ethylene oxide and CO_2 [18]. Furthermore, in the presence of an IL, the decarboxylation can be carried out in a homogeneous way. The catalytic activity of 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) was evaluated first because [BMIm]Cl, like NaCl, is also an ionic compound consisting of a cation and an anion in a 1:1 ratio, and because the Cl^- of [BMIm]Cl is a strong nucleophile. However, contrary to our expectation, no noticeable improvement in the selectivity or yield of glycidol was observed with the use of [BMIm]Cl, implying that either the acidity of the cation or the basicity of the anion for the IL is not optimized for the decarboxylation of GLC. To find more selective ILs through a suitable combination of cations and anions, the decarboxylation of GLC was undertaken in the presence of various [BMIm]-based ILs. As can be seen in Fig. 1, [BMIm]NO_3 and [BMIm]I showed considerably higher yields and selectivities of glycidol than did other ILs. As in the case of sodium metal salts, 1-butyl-3-methylimidazolium acetate ([BMIm]AcO) with a strongly basic anion, $CH_3CO_2^-$, afforded glycidol in a much lower yield of 39.3% compared with that of [BMIm]Cl. Similar to $NaBF_4$ and $NaPF_6$, [BMIm]BF_4 and [BMIm]PF_6 with a non-coordinating anion showed negligible activity toward decarboxylation. Such a strong dependence of glycidol yield and selectivity on the type of anion again suggests that the degree of interaction between the anion and the hydroxyl groups of GLC and glycidol through the hydrogen-bond is the most important factor in determining the activity of ILs and the selectivity of glycidol.

In order have a better insight into the anion effect on the decarboxylation of GLC, the concept of hydrogen-bond basicity (β value) of ILs, a Kamlet–Taft solvent parameter determined by the nature of the anion of an IL, was introduced. Based on the reported β values of the ILs [18–21], the correlation of the yield of glycidol with the β value was plotted. As can be seen in Fig. 1, the yield of glycidol increased with increasing β values up to 0.8, but decreased thereafter. On the whole, ILs with a β value in the range 0.6–0.8 showed higher glycidol yields than those with β values higher than 0.8 or lower than 0.6. On the contrary, conversions of GLC remained almost constant at over 95% as long as the β value was above 0.6. From these results, it is clear that, for an IL to be active and selective, the β value of the anion should be in the range of approximately 0.6–0.8.

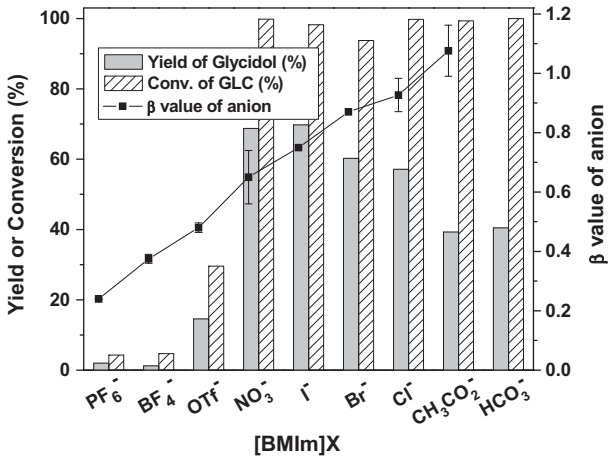


Fig. 1. Correlation of Kamlet–Taft hydrogen-bond basicity (β) of the anion of ILs with their activity for the decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, molar ratio of IL/GLC = 0.005, T = 175 °C, P = 2.67 kPa, t = 45 min. * β values were obtained from the references [19–22].

In order to investigate the effect of cation, the catalytic performance of four different ILs with a nitrate anion, including [BMIm]NO_3, 1-butyl-2,3-dimethylimidazolium nitrate ([BDMIm]NO_3), N-methyl-N-propylpyrrolidinum nitrate ([MPPyr]NO_3), and tetra-*n*-butylammonium nitrate ([Bu_4N]NO_3), was compared. As can be seen in Table 3, the conversion of GLC was almost quantitative irrespective of the ILs, implying that the ILs with a NO_3^- is sufficiently active enough to complete the decarboxylation of GLC, irrespective of the types of cations. In contrast, the yield and selectivity of glycidol were slightly affected by the type of the cation. [BDMIm]NO_3 afforded the higher yield and selectivity of glycidol than [BMIm]NO_3, whereas [MPPyr]NO_3 and [Bu_4N]NO_3 exhibited lower glycidol yields and selectivity than [BDMIm]NO_3. It is particularly notable that [BDMIm]NO_3 showed higher selectivity to glycidol than [BMIm]NO_3. The reason for the higher selectivity with [BDMIm]NO_3 is not clear, but the reduction of the acidity of the imidazolium cation by the substitution of the acidic C(2)–H with the electron donating methyl group seems to decrease the cation–anion interaction, consequently resulting in the increase in the β value of NO_3^-. However, considering the higher glycidol yield and selectivity with [BDMIm]NO_3 than those with [BMIm]NO_3 having the β value in the range 0.6–0.8, it is likely that the increase in the anion β value is small, because the β value should not exceed 0.8 for the IL to be selective toward the decarboxylation of GLC (*vide supra*). One might suspect that the formation of side products could be related to the interaction between the cation and glycidol through the epoxy oxygen atom. However, comparison of the FT-IR spectra for the interactions of glycidol with [BMIm]NO_3 and [BDMIm]NO_3 clearly indicated that the interactions of cations with glycidol were almost negligible because the C–O (epoxy oxygen) stretching frequency of glycidol was not changed appreciably by the substitution of the acidic C(2)–H with the methyl group (see Fig. S1 in Supporting information).

It was anticipated that [Bu_4N]NO_3 and [MPPyr]NO_3 could exhibit similar or higher glycidol selectivity than [BDMIm]NO_3 because the acidities of $[Bu_4N]^+$ and $[MPPyr]^+$ are weaker than that of $[BDMIm]^+$, due to the absence of acidic hydrogen atom. However, contrary to our expectation, [Bu_4N]NO_3 and [MPPyr]NO_3 showed considerably lower glycidol yields and selectivities than [BDMIm]NO_3. It is presumed that the β values of NO_3^- in these ILs are higher than 0.8.

Table 3
Effect of cation of ILs on the decarboxylation of GLC.[a]

Entry	Cation	C (%)	Y (%)	S (%)	TOF (h^{-1})
1	[BMIm]	99.8	68.7	68.9	183
2	[BDMIm]	99.1	73.2	73.9	195
3	[Bu_4N]	99.3	64.2	63.8	171
4	[MPPyr]	100	58.9	58.9	157

[a] *Reaction conditions*: GLC = 169 mmol, molar ratio of IL/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.

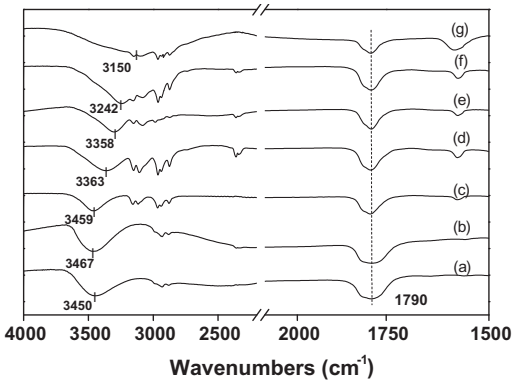


Fig. 2. FT-IR spectra showing the interactions of GLC with ILs: (a) GLC, (b) GLC–[BMIm]BF_4, (c) GLC–[BMIm]OTf, (d) GLC–[BMIm]NO_3, (e) GLC–[BMIm]I, (f) GLC–[BMIm]Cl, and (g) GLC–[BMIm]CH_3CO_2. The molar ratio of GLC to IL was set at 1.

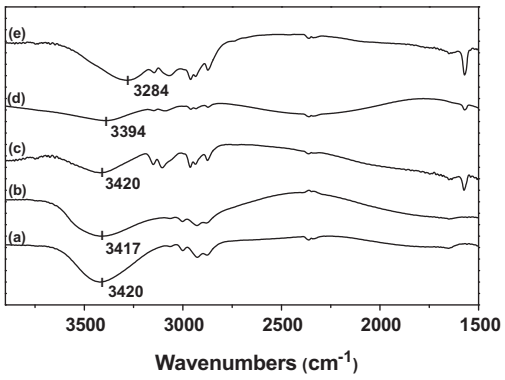


Fig. 3. FT-IR spectra showing the interactions of glycidol with ILs: (a) glycidol, (b) glycidol–[BMIm]BF_4, (c) glycidol–[BMIm]NO_3, (d) glycidol–[BMIm]I, and (e) glycidol–[BMIm]Cl. The molar ratio of glycidol to IL was set at 1.

3.4. FT-IR studies

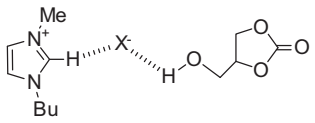
The effect of anions on the activity of ILs toward the decarboxylation of GLC was further demonstrated by FT-IR studies. As can be seen in Fig. 2, upon contact of GLC with [BMIm]NO_3 and [BMIm]I bearing an anion with a β value of around 0.70, the absorption band centered at 3450 cm^{-1} corresponding to the hydroxyl group of free GLC moved to lower frequencies of 3363 and 3358 cm^{-1}, respectively. The O–H stretching frequency shift was even more pronounced when GLC was interacted with [BMIm]Cl and [BMIm]AcO with a more basic anions having a β values of 0.93 and 0.99, respectively. The peaks corresponding to the hydroxyl group of GLC appeared at 3242 cm^{-1} for [BMIm]Cl and at 3150 cm^{-1} for [BMIm]AcO, suggesting that the degree of interaction between the hydroxyl group and the anions of an ILs is of pivotal importance in determining the activity of the ILs and the yield and selectivity of glycidol.

On the contrary, the O–H stretching frequency of GLC at 3450 cm^{-1} shifted to a higher frequency of 3467 cm^{-1} upon interaction with [BMIm]BF_4, indicating that there is no interaction between the hydroxyl group of GLC and BF_4^-. The higher frequency shift can be ascribed to the weakening of hydrogen-bonding interactions between GLC molecules due to the dilution with [BMIm]BF_4, thereby resulting in the increase in the O–H bond strength.

In consideration of the experimental and FT-IR results, it is obvious that the activation of the O–H bond of GLC by the anion of an IL through hydrogen-bonding interaction is a prerequisite for GLC to be decarboxylated as depicted in Scheme 2. The stronger the interaction is, the easier the decarboxylation is.

Although most of the ILs tested was highly active for the decarboxylation of GLC, the performance of these ILs still needs to be greatly improved in terms of yield and selectivity of glycidol. It is postulated that the low yield and selectivity of glycidol are resulted from the activation of the hydroxyl group of glycidol by the anions of ILs, which could lead to the formation of side products through the dimerization and oligomerization of glycidol [23,24]. To confirm our postulate, the interactions of glycidol and ILs were investigated by FT-IR spectroscopy. As can be seen in Fig. 3, substantial interactions were observed between ILs and glycidol, although the interactions were much weaker than those with GLC.

Therefore, for an IL to be active and selective, the interaction of the anion of the IL with GLC should be strong enough, and the interaction of the anion of the IL with glycidol must be sufficiently weak. This is probably the reason why [BMIm]NO_3 and [BMIm]I bearing an anion with a medium β value exhibit selectivity higher than that of other ILs.



Scheme 2. Hydrogen-bonding interaction between [BMIm]X and GLC.

3.5. Effect of catalyst loading

The effect of catalyst loading on the decarboxylation of GLC was investigated for the [BMIm]NO_3- and [BMIm]Cl-catalyzed reactions. As can be seen in Fig. 4, for the decarboxylation in the presence of [BMIm]NO_3, the conversion of GLC quantitative at the [BMIm]NO_3/GLC molar ratio of 0.005. On the contrary, the glycidol yield and selectivity reached the maximum values of approximately 69% at the molar ratio of 0.0025. Any change in yield and selectivity was not observed on further increase in the molar ratio.

For the [BMIm]Cl-catalyzed decarboxylation shown in Fig. 5, the conversion of GLC reached 100% at the [BMIm]Cl/GLC molar ratio of 0.0025 and remained quantitative on further increase in the molar ratio. Unlike the case of the [BMIm]NO_3-catalyzed reaction, however, the yield of glycidol decreased gradually above the molar ratio of 0.0025. It is likely that the interaction of glycidol with Cl^-, one of the strongest basic anions, is more accelerated with the increasing concentration of [BMIm]Cl, thereby promoting the

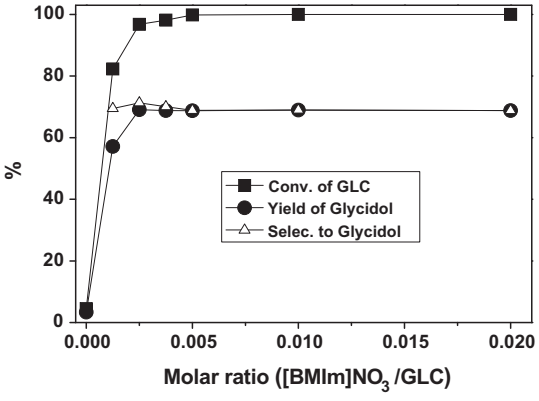


Fig. 4. Effect of [BMIm]NO_3/GLC molar ratio on the decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, T = 175 °C, P = 2.67 kPa, t = 45 min.

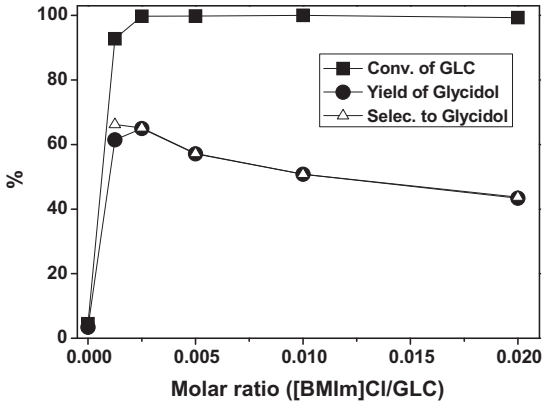


Fig. 5. Effect of [BMIm]Cl/GLC molar ratio on the decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, T = 175 °C, P = 2.67 kPa, t = 45 min.

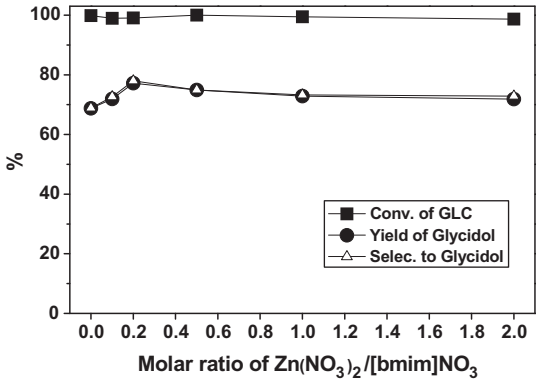


Fig. 7. Effect of added $Zn(NO_3)_2$ on the $[BMIm]NO_3$-catalyzed decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, molar ratio of $[BMIm]NO_3$/GLC = 0.005, T = 175 °C, P = 2.67 kPa, t = 45 min.

secondary reactions of glycidol such as dimerization and oligomerization.

3.6. Effect of added zinc salt

Kim et al. reported that [EMIm]Br promotes the decomposition of ethylene carbonate into ethylene oxide and CO_2, and that the rate of decomposition increased greatly when $ZnCl_2$ was co-present with [EMIm]Br at a 1:2 M ratio because of the formation of a Zn-containing IL, $[EMIm]_2ZnCl_2Br_2$ [18]. It was anticipated that the co-use of a zinc salt like $ZnCl_2$ or $Zn(NO_3)_2$ with $[BMIm]NO_3$ would give similar synergy effect to that observed in the decomposition of ethylene carbonate. As can be seen in Fig. 6, the yield of glycidol increased from 68.7% to 74.3% when 0.2 M equivalent of $ZnCl_2$ was used along with $[BMIm]NO_3$. However, on further increase in the molar ratio of $ZnCl_2$/$[BMIm]NO_3$ above 0.2, the yield of glycidol and the conversion of GLC dropped rapidly. Moreover, the catalytic activity of $[BMIm]NO_3$ was completely quenched at the $ZnCl_2$/$[BMIm]NO_3$ molar ratio of 2. As in the case of [EMIm]Br and $ZnCl_2$, there seems to be a reaction between $[BMIm]NO_3$ and Lewis acidic $ZnCl_2$ under the experimental condition, forming $[BMIm]_2Zn(NO_3)_2Cl_2$-like species. Once $[BMIm]NO_3$ is complexed with $ZnCl_2$, the β value of NO_3^- gets greatly reduced due to the strong electron-withdrawing effect of Cl ligands, thereby resulting in the decrease in GLC conversion and glycidol yield. The increase in glycidol yield with the addition of 0.2 equivalent of $ZnCl_2$ with respect to $[BMIm]NO_3$ can be rationalized to a certain extent from the experimental results shown in Fig. 4, which shows that the yield of glycidol at the $[BMIm]NO_3$/GLC molar ratio of 0.0025 is higher than that at the molar ratio of 0.005. Considering that the maximum amount of $[BMIm]NO_3$ to be consumed in the formation of the completely inactive species, $[BMIm]_2Zn(NO_3)_2Cl_2$ by the reaction with 20 mol% of $ZnCl_2$ is 40 mol% of the initial loading of $[BMIm]NO_3$, it is conceivable that 60 mol% of $[BMIm]NO_3$ is survived. Therefore, the glycidol yield obtained at the $[BMIm]NO_3$/GLC of 0.005 and at the $ZnCl_2$/$[BMIm]NO_3$ molar ratio of 0.2 would be very similar to that achieved at the $[BMIm]NO_3$/GLC of 0.003 in the absence of $ZnCl_2$.

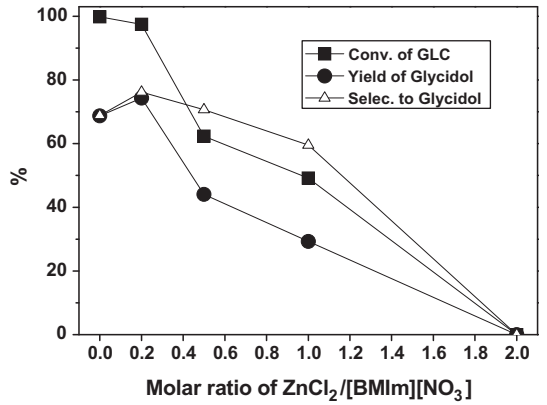


Fig. 6. Effect of added $ZnCl_2$ on the $[BMIm]NO_3$-catalyzed decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, molar ratio of $[BMIm]NO_3$/GLC = 0.005, T = 175 °C, P = 2.67 kPa, t = 45 min.

As can be seen in Fig. 7, a synergy effect was observed with the addition of $Zn(NO_3)_2$ up to the molar ratio of $Zn(NO_3)_2$/$[BMIm]NO_3$ at 0.2, resulting in the increase in the glycidol yield from 68.7% to 77.2%. However, unlike the addition of $ZnCl_2$, the drop in the yield of glycidol with the increase in the $Zn(NO_3)_2$/$[BMIm]NO_3$ molar ratio was not pronounced. The yield of glycidol decreased from 77.2% to 71.9% with the variation of the molar ratio from 0.2 to 2. This can be attributed to the much weaker Lewis acidity of $Zn(NO_3)_2$ than that of $ZnCl_2$. The formation of $[BMIm]_2Zn(NO_3)_4$ can also be conceivable from the interaction of $[BMIm]NO_3$ with $Zn(NO_3)_2$, but the change in β value of NO_3^- upon complexation seems not be significant.

The reason for the increase in the glycidol yield with the addition of 0.2 M equivalent of $Zn(NO_3)_2$ to the amount of $[BMIm]NO_3$ can be explained by the higher frequency shift of the O–H stretching band. As can be seen in Fig. 8, the O–H stretching frequency shifted from 3363 to 3400 cm^{-1} with the addition of 0.2 M equivalent of $Zn(NO_3)_2$, suggesting that the hydrogen-bonding interactions between NO_3^- of $[BMIm]NO_3$ with the hydroxyl groups of GLC and glycidol are weakened by the interaction of NO_3^- with the Lewis acidic $Zn(NO_3)_2$.

This is in contrast to the previously reported results on the decarboxylation of ethylene carbonate. The highest decomposition was achieved at the $ZnCl_2$/$[BMIm]Br$ molar ratio of 0.5, at which level the basicity of Br^- or Cl^- becomes the highest [18]. Such a discrepancy seems to have originated from the lack of an additional hydroxyl group in the ethylene oxide produced. In the decomposition of ethylene carbonate, secondary reactions of ethylene oxide would not be possible because any functional group to interact with basic Br^- or Cl^- is not present in the ethylene oxide molecule.

As listed in Table 4, other Lewis acids like $MgCl_2$, $FeCl_3$, and $AlCl_3$ were found to exhibit similar synergy effect to that observed with $ZnCl_2$ when they were used together along with $[BMIm]NO_3$ with the molar ratio of Lewis acid/$[BMIm]NO_3$ at 0.2. As mentioned above, the anion basicity of NO_3^- seems to be weakened by the presence of a Lewis acid, thereby resulting in the decrease in the interaction between NO_3^- and the hydroxyl group of glycidol.

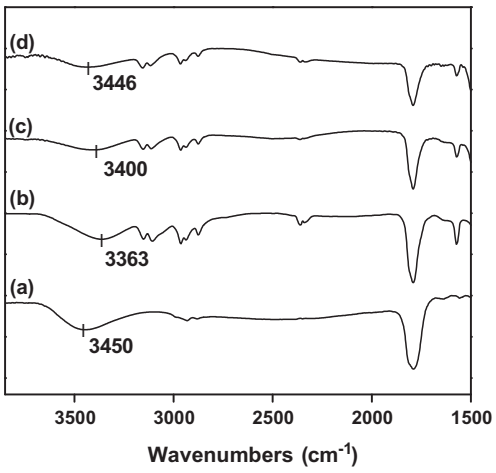


Fig. 8. FT-IR spectra of showing the effect of added $ZnCl_2$ on the $[BMIm]NO_3$-catalyzed decarboxylation of GLC: (a) GLC, (b) GLC/$[BMIm]NO_3$ (1/1), (c) GLC–$[BMIm]NO_3/Zn(NO_3)_2$ (1/1/0.2), and (d) GLC/$[BMIm]NO_3/Zn(NO_3)_2$ (1/1/0.5). The numbers in the parentheses are the molar ratios.

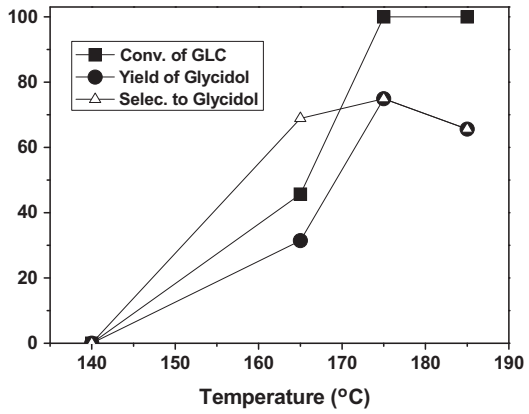


Fig. 9. Effect of reaction temperature on the decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, molar ratio of $[BMIm]NO_3$/GLC = 0.005, molar ratio of $Zn(NO_3)_2/[BMIm]NO_3$ = 0.2, P = 2.67 kPa, t = 45 min.

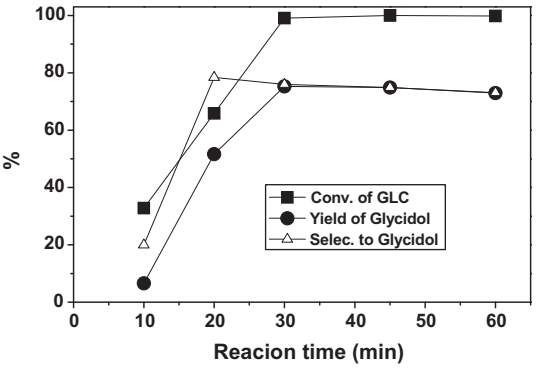


Fig. 10. Effect of reaction time on the decarboxylation of GLC. Reaction conditions: GLC = 169 mmol, molar ratio of $[BMIm]NO_3$/GLC = 0.005, molar ratio of $Zn(NO_3)_2/[BMIm]NO_3$ = 0.2, P = 2.67 kPa, T = 175 °C.

Table 4
Effect of added metal salts on the $[BMIm]NO_3$-catalyzed decarboxylation of GLC.[a]

Entry	Catalyst	C (%)	Y (%)	S (%)	TOF (h^{-1})
1	$ZnNO_3$	99.0	77.2	78.0	206
2	$ZnCl_2$	97.5	74.3	76.2	198
3	$FeCl_3$	99.8	73.2	73.3	195
4	$MgCl_2$	99.4	74.5	74.9	199
5	$AlCl_3$	99.9	73.8	73.9	197

[a] Reaction conditions: GLC = 169 mmol, molar ratio of $[BMIm]NO_3$/GLC = 0.005, molar ratio of metal chloride/$[BMIm]NO_3$ = 0.2, 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 $[BMIm]NO_3$/h.

3.7. Effects of reaction temperature and time

The effects of reaction temperature and time were also investigated using a catalyst system, $Zn(NO_3)_2/[BMIm]NO_3$ (0.2/1). As can be seen in Fig. 9, both the conversion of GLC and the yield of glycidol increased with the temperature rise and reached a maximum at 175 °C. However, further increases in the temperature only resulted in the decrease in the selectivity to glycidol.

The effect of the reaction time was also investigated at 175 °C. As can be seen in Fig. 10, the decarboxylation was completed in 30 min, indicating that the decarboxylation of GLC proceeded very rapidly in the presence of $Zn(NO_3)_2/[BMIm]NO_3$ (0.2/1).

3.8. Effect of solvent on the decarboxylation of GLC for the batch and continuous reactions

In principle, the formation of side products can be suppressed to a great extent through a suitable combination of cations and anions of ILs. However, the optimal combination seems hard to find. Therefore, the best way to reduce the formation of side products is probably to carry out the decarboxylation reaction in a continuous way using a solvent to minimize the contact between the IL and glycidol while simultaneously removing glycidol as soon as it forms. With this in mind, batch and continuous reactions for the decarboxylation of GLC were conducted in a high-boiling solvent using a catalytic system consisting of $Zn(NO_3)_2$ and $[BMIm]NO_3$ at the molar ratio of 0.2:1. In a 250 mL three-necked flask equipped with a condenser, electrical heater, and a thermocouple, a high-boiling solvent solvent (50 g), $[BMIm]NO_3$ (0.13 g), and $Zn(NO_3)_2$ (0.025 g) were loaded and then heated to 175 °C at 2.67 kPa. For the batch reaction, GLC (33.6 g) was added from the beginning along with the solvent and was decarboxylated at 175 °C for 2 h. For the continuous reactions, GLC was introduced into the reaction flask at 175 °C at a flow rate of 0.2 mL (0.28 g, 2.37 mmol/min) over a period of 2 h using an HPLC pump. In order to complete the reaction, the mixture was reacted further at that temperature for 30 min. Glycidol was removed from the reaction system as soon as it formed by performing the reaction under a reduced pressure.

Table 5
Effect of solvent on the decarboxylation of GLC for the batch and continuous reactions.

Entry	Solvent	C (%)	Y (%)	S (%)	TOF (h^{-1})
1[a]	DMPEG 350	99.7	83.2	83.5	128
2[b]	DMPEG 350	100	98.2	98.2	150
3[a]	Dibenzyl ether	100	82.1	82.1	123
4[b]	Dibenzyl ether	99.4	97.3	97.9	148
5[a]	Dibutyl phthalate	99.8	84.4	84.6	129
5[b]	Dibutyl phthalate	100	96.9	96.9	148

C = GLC conversion, Y = glycidol yield, S = glycidol selectivity, TOF (h^{-1}) = moles of glycidol produced/moles of $[BMIm]NO_3$/h.

[a] *Batch reaction*: GLC = 284 mmol, solvent 50 g, catalyst = $Zn(NO_3)_2$–$[BMIm]NO_3$, $[BMIm]NO_3$ (0.64 mmol, 0.13 g), molar ratio of $Zn(NO_3)_2/[BMIm]NO_3$ = 0.2, molar ratio of $[BMIm]NO_3$/GLC = 0.0025, T = 175 °C, P = 2.67 kPa, t = 2.5 h.

[b] Continuous reaction: total GLC feed = 284 mmol, GLC feed rate = 0.2 mL(2.37 mmol)/min, solvent 50 g, catalyst = $Zn(NO_3)_2$–$[BMIm]NO_3$, $[BMIm]NO_3$ (0.64 mmol, 0.13 g), molar ratio of $Zn(NO_3)_2/[BMIm]NO_3$ = 0.2, T = 175 °C, P = 2.67 kPa, t = 2.5 h.

As can be seen in Table 5, the use of high-boiling solvents such as glycol dimethyl ether (DMPEG, MW = 350), dibenzyl ether, and dibutyl phthalate increased the yield and selectivity of glycidol for both batch and continuous reactions. However, the effect of solvent was more effective for the continuous reactions. For example, the analysis of the products in a receiver and the flask for the continuous reaction in DMPEG demonstrated that the decarboxylation of GLC was quantitative and the yield and selectivity of glycidol were as high as 98% (entry 2). Among solvents tested, DMPEG afforded the highest glycidol yield, but difference in glycidol yield with the solvent was not great.

In order to test the catalyst longevity, the continuous reaction was conducted 175 °C for 40 h in DMPEG (50 g) using the catalytic system consisting of [BMIm]NO_3 (0.26 g) and $Zn(NO_3)_2$ (0.049 g). The flow rate of GLC was controlled at 0.2 mL/min (0.28 g, 2.37 mmol/min) throughout the reaction. Every 4 h, the product in the receiver was transferred into the 100-mL sampling cylinder by opening the valve between them and was weighed and analyzed. Fig. 11 shows the change of the molar ratio of the glycidol recovered/GLC injected for 4 h. As can be seen in Fig. 11, the molar ratio of glycidol/GLC was maintained in the range 0.97–0.98 for the first seven samples taken every 4 h, but the molar ratio started to decrease gradually thereafter down to 0.92. The analysis of the reaction mixture in the flask after the 40 h reaction showed that approximately 4.7 mol% of GLC was converted to the side products. These results demonstrate that the catalytic system, [BMIm]NO_3/$Zn(NO_3)_2$, is quite stable under the experimental condition. The TOF (moles of glycidol produced/moles of [BMIm]NO_3/h) and TON (moles of glycidol produced/moles of [BMIm]NO_3) after 40 h of the continuous reaction were calculated to be 107 and 4.3×10^3, respectively.

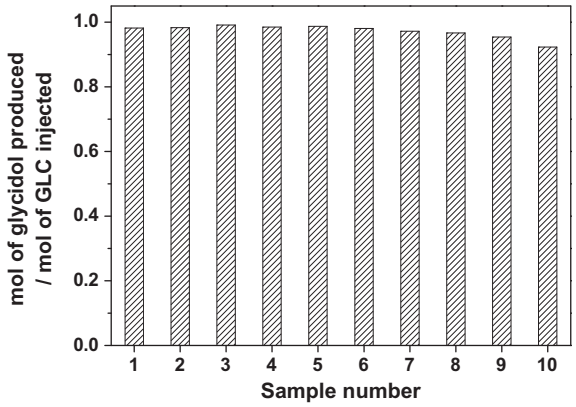


Fig. 11. Change of the molar ratio of glycidol collected/GLC injected with the samples taken every 4 h. Reaction conditions: GLC feed rate = 0.2 mL (2.37 mmol)/min, [BMIm]NO_3 = 0.26 g(1.29 mmol), molar ratio of $Zn(NO_3)_2$/[BMIm]NO_3 = 0.2, P = 2.67 kPa, T = 175 °C, t = 40 h, solvent = DMPEG 350. Glycidol collected in the receiver was withdrawn every 4 h for analysis.

3.9. Computational calculations on the mechanism for the formation of glycidol

The mechanism for the decarboxylation of GLC was theoretically investigated using [EMIm]NO_3 as the catalyst. Fig. 12 shows the optimized structures for the interactions of [EMIm]NO_3 with GLC. The computational calculations show that the decarboxylation of GLC to glycidol proceeds in two steps. The first step is the NO_3-assisted ring-opening of GLC and the ring closure, forming a 3-membered ring. The driving force for the ring-opening seems to be the strong hydrogen-bonding interaction between the O atom of the NO_3^- and the H atom of the hydroxyl group of GLC, as revealed from the short H–O distance of 1.40 Å in the optimized structure of the first transition state (TS1). With such strong interaction, the O–H bond can be cleaved and the resulting CH_2O^- be-

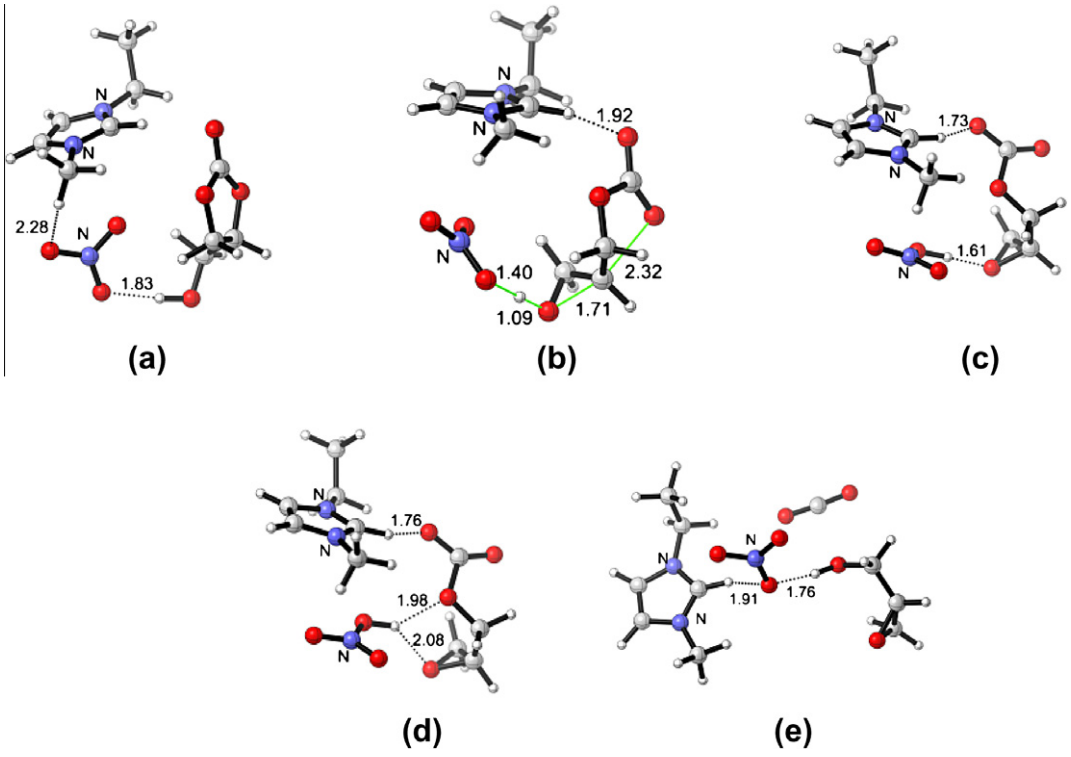


Fig. 12. Optimized structures of reaction intermediates and transition states involved in the [EMIm]NO_3-assisted decarboxylation reaction of GLC: (a) reactant (ΔG_r = 0 kcal mol^{-1}), (b) TS1 ($\Delta G^{\ddagger}_{TS1}$ = 37.4 kcal mol^{-1}), (c) intermediate (ΔG_i = 26.3 kcal mol^{-1}), (d) TS2 ($\Delta G^{\ddagger}_{TS2}$ = 28.8 kcal mol^{-1}), and (e) product (ΔG_p = 10.2 kcal mol^{-1}). The Gibbs free energy of formation (ΔG) and transition state energy ($\Delta G^{\ddagger}$) are relative values with respect to that of the reactant.

comes highly nucleophilic enough to interact with the neighboring carbon atom, forming C–O bond as manifested by the C–O bond distance of 1.71 Å. In the optimized structure of the intermediate species, it is worth to note that there is also a strong interaction between the C(2)–H of the $[EMIm]^+$ and the carbonate group (O–H bond: 1.73 Å), suggesting that the intermediate species is stabilized to a certain extent by the hydrogen-bonding interaction with the imidazolium ring. The intermediate species seems to be further stabilized via the interaction between the H atom of the dissociated HNO_3 and the ether oxygen atom. The activation energy of the first transition state ($\Delta G^{\ddagger}_{TS1}$) and the Gibbs free energy of formation of the intermediate species (ΔG_i) were calculated as 37.4 and 26.3 kcal mol^{-1}, respectively. It is interesting to note that the intermediate species has an ionic-liquid-type structure consisting of $[BMIm]^+$ and carbonate anion.

The second step is the proton transfer from HNO_3 to an oxygen atom of the carbonate group along with the simultaneous loss of CO_2. It is likely that the transformation of the intermediate species proceeds immediately because the activation energy for the second step is only 2.5 kcal/mol ($\Delta G^{\ddagger}_{TS2} - \Delta G_i$). The activation energy of the second transition state ($\Delta G^{\ddagger}_{TS2}$) and the Gibbs free energy of formation of the product (ΔG_p) were calculated as 28.8 and 10.2 kcal mol^{-1}, respectively. As a whole, the computational results are in good agreement with those obtained from the decarboxylation experiments and spectroscopic analysis.

4. Conclusions

In summary, decarboxylation of GLC was conducted using various kinds of sodium salt and ILs. The experimental and spectroscopic results clearly showed that the effect of anions was more pronounced than that of cations. The correlation of the catalytic performance of an IL with the β value of the anion demonstrated that the β value of the anion should be in the range of 0.60–0.80 for the IL to be active and selective for the decarboxylation of GLC. It was possible to enhance the selectivity of glycidol to a certain extent by the co-use of Lewis acidic $Zn(NO_3)_2$ with $[BMIm]NO_3$. The yield of glycidol was greatly increased up to 98% when a decarboxylation was carried out using a high-boiling solvent in a continuous way.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.10.015.

References

[1] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C.D. Pina, Angew. Chem. Int. Ed. 46 (2007) 4434.
[2] J.A. Kenar, Lipid Technol. 19 (2007) 249.
[3] C.H.C. Zhou, J.N. Beltramini, Y.X. Fan, G.Q.M. Lu, Chem. Soc. Rev. 37 (2008) 527.
[4] C. Hammond, J.A. Lopez-Sanchez, M.H. Ab Rahim, N. Dimitratos, R.L. Jenkins, A.F. Carley, Q. He, C.J. Kiely, D.W. Knight, G.J. Hutchings, Dalton Trans. 40 (2011) 3927.
[5] J.H. Park, J.S. Choi, S.K. Woo, S.D. Lee, M. Cheong, H.S. Kim, H. Lee, Appl. Catal. A: Gen. 433 (2012) 35.
[6] M. Pagliaro, M. Rossi, Esterification, in: The Future of Glycerol, New Usages for a Versatile Raw Material, RSC Green Chemistry Book Series, RSC Publishing, Cambridge, 2010, p. 108.
[7] O. Gómez-Jiménez-Aberasturi, J.R. Ochoa-Gómez, A. Pesquera-Rodríguez, C. Ramírez-López, A. Alonso-Vicario, J. Torrecilla-Soria, J. Chem. Technol. Biotechnol. 85 (2010) 1663.
[8] N. Mizuno, S. Hikichi, K. Yamaguchi, S. Uchida, Y. Nakagawa, K. Uehara, K. Kamata, Catal. Today 117 (2006) 32.
[9] W.F Richey, Chlorohydrins, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., vol. 6, John Wiley, New York, 1993, p. 140.
[10] J.W. Yoo, Z. Moulounguí, A. Gaset, Organisation Nationale Interprofessionelle des Oleagineux, US 6316641 B1, 2001.
[11] Y. Seki, T. Sasa, H. Takeuchi, M. Uno, M. Namba, Kao Corp., US 2011/0015414 A1, 2011.
[12] H.S. Kim, J.J. Kim, H. Kim, H.G. Jang, J. Catal. 220 (2003) 44.
[13] J. Peng, Y. Deng, New J. Chem. 25 (2001) 639.
[14] B. Mokhtarani, A. Sharifi, H.R. Mortaheb, M. Mirzaei, M. Mafi, F. Sadeghian, J. Chem. Thermodyn. 41 (2009) 1432.
[15] Y.S. Choi, Y.N. Shim, J. Lee, C.S. Hong, M. Cheong, H.S. Kim, H.G. Jang, J.S. Lee, Appl. Catal. A: Gen. 404 (2011) 87.
[16] M.J. Frisch, et al., Gaussian 09. Revision A.1, Gaussian Inc., Wallingford, CT, USA, 2009 (see SI for details).
[17] M. Uno, M. Okutsu, Kao Corp., EP 2,028,181 A1, 2009.
[18] H.S. Kim, P. Jelliarko, J.S. Lee, S.Y. Lee, H. Kim, S.D. Lee, B.S. Ahn, Appl. Catal. A: Gen. 288 (2005) 48.
[19] P.G. Jessop, D.A. Jessop, D. Fu, L. Phan, Green Chem. 14 (2012) 1245.
[20] R. Lungwitx, S. Spange, New J. Chem. 32 (2008) 392.
[21] L. Crowhurst, P.R. Mawdsley, J.M. Perez-Arlandis, P.A. Salter, T. Welton, Phys. Chem. Chem. Phys. 5 (2003) 2790.
[22] M.A.A. Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N.H. Hassan, J.P. Hallett, P.A. Hunt, H. Niedermeyer, J.M. Perez-Arlandis, M. Schrems, T. Welton, R. Wilding, Phys. Chem. Chem. Phys. 13 (2011) 16831.
[23] G. Rokicki, P. Rakoczy, P. Parzuchowski, M. Sobiecki, Green Chem. 7 (2005) 529.
[24] S.R. Sandler, F.R. Berg, J. Polym. Sci. 4 (1966) 1253.