

Efficient synthesis of glycerol carbonate/glycidol using 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) based ionic liquids as catalyst†

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Transesterification of dimethyl carbonate with glycerol to glycerol carbonate has been catalyzed efficiently using basic ionic liquids as catalysts. Activity of all the ILs tested is very high and the best result (96% conversion with 82% selectivity to glycerol carbonate and 18% selectivity to glycidol) was obtained using IL1 as catalyst. The effect of catalyst loading has significant influence on the selectivity pattern. The higher activity of the ionic liquid is explained with a plausible mechanism based on the co-operative effect of both cation and anion.

Introduction

Continuous reduction in fossil fuel resources and increasing concerns about climate change are major issues for the sustainable development of society. The use of renewable resources is one of the solutions for the aforementioned issues. In the last couple of decades much attention has been devoted to applying green catalytic processes to convert biorenewable feed stocks to commodity chemicals and clean fuels. Glycerol (GLY), one of the renewable resources, is obtained as a by-product from the hydrolysis of fats, soap-manufacturing processes, and production of biodiesel.¹ Biodiesel manufacture is also increasing day-by-day and relatively cheap GLY is expected to be available in large quantities. One of the major bottlenecks in the enhancement of biodiesel production is the utilization of GLY, which needs to be converted into value added products in an economical way. Research efforts to find new applications for conversion of GLY as a low-cost feed stock for the synthesis of functional derivatives have led to a number of processes for converting GLY selectively to value added products.² Glycerol carbonate (GC) and glycidol (GD) obtained from GLY are important products with a wide range of applications in the fields of pharmaceutical, membrane and polymer industries for the production of polyesters, polycarbonates,

polyurethanes, polyamides, surfactants, lubricating oils and other chemicals.³ The reaction of phosgene with GLY is the conventional method for the synthesis of GC.⁴ However, the toxicity of phosgene is the major problem with the conventional method. In order to overcome this drawback of the conventional method, four new routes have been developed for conversion of GLY to GC. Namely, oxidative carbonylation of GLY, direct carboxylation of GLY using CO₂, reaction of GLY with urea and transesterification of dialkyl carbonate with GLY. Among all the routes, the route based on the transesterification of dialkyl carbonate with GLY is one of the most popular. Numerous heterogeneous (metal oxides, mixed metal oxides, hydroxalicates, supported hydroxyapatite and Sn-complexes) as well as homogeneous (inorganic metal salts, quaternary ammonium salts and ionic liquids) catalysts have been proposed for this route.³ Among the catalysts reported Sn-complexes and basic ionic liquids showed high activity for GC synthesis, but their catalytic activities expressed as turnover number (TON) were in the range of 100–200 (TON = 200 for 1,3-dichlorostannoxane at 100 °C after 120 minute,⁵ TON = 100 for BMIM-2-CO₂ at 74 °C after 80 min⁶ and TON = ~100 for [TMA][OH] at 80 °C after 90 min⁷).

From the literature it was observed that the maximum TON reported was 200 and also the scope of catalysts investigated is limited. In particular, the use of basic ionic liquids as catalysts is very limited and there is a scope for use of other basic ionic liquids as catalysts for this reaction.

Herein, we report our results on the use of DBU based ionic liquids as basic catalysts for transesterification of dimethyl carbonate (DMC) with GLY. To the best of our knowledge, this is the first report on the use of diazabicyclo [5.4.0] undec-7-ene (DBU) based ionic liquids as catalysts for GC/GD synthesis.

Experimental section

Chemicals

Glycerol (99%), glycidol (96%), glycerol carbonate (95%) and 1,8-diazabicyclo [5.4.0] undec-7-ene (99%) were purchased from

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Aldrich, dimethyl carbonate (99%) from Spectrochem, India, methanol (99%) from Merck, India and propylene glycol (99%) from Loba Chemie, India. All the chemicals were used as received from suppliers.

The synthesized ionic liquids were characterized by means of nuclear magnetic resonance (NMR) spectroscopy, experiments were carried out on a Bruker Avance 400 wide bore spectrometer equipped with a superconducting magnet with a field of 9.4 T. The operating frequency for ^{13}C was 75.4 MHz. The ILs were also characterized by FT-IR spectroscopy on an Agilent Technologies Cary 600 series FT-IR spectrometer.

Typical procedure for the ionic liquids preparation

DBU derived basic ionic liquids have been prepared by bubbling CO_2 into the mixture of DBU and alcohols such as methanol, propylene glycol or GLY. Molar amounts of DBU and alcohols used were 1 : 1, 2 : 1 and 3 : 1, respectively, for the synthesis of IL1, IL2 and IL3 (1 : 1 molar amount of DBU and methanol for IL1, 2 : 1 molar amount of DBU and propylene glycol for IL2 and 3 : 1 molar amount of DBU and GLY for IL3). All the ionic liquids were prepared as per the procedure described earlier.⁸ From the literature it was observed that the ILs prepared from triol-like GLY is mostly present in monocarbonate form, indicating incomplete conversion of hydroxyl groups.⁸ However, with mono-ols like methanol the conversion was almost quantitative, probably because of the high polarity of the alcohols.⁹ The typical experimental procedure for preparation of IL3 is given below.

DBU-glyceryl carbonate IL

The DBU glyceryl carbonate ionic liquid was prepared by bubbling CO_2 through a mixture of DBU-GLY (molar ratio 3 : 1). DBU (6 g) 39.41 mmol and GLY (1.2 g) 13.13 mmol were used for preparing a 3 : 1 molar mixture. Thereafter, a narrow-gauge glass tube was inserted and CO_2 was bubbled through the liquid until there was no more weight increase. The reaction was notably exothermic and the solution was stirred mechanically throughout the bubbling cycle. During the course of the reaction the liquid became viscous. Other ionic liquids were also prepared starting from DBU and other alcohols such as methanol and propylene glycol as reactants by following the same procedure. All the ionic liquids prepared were characterized by NMR and IR analysis.

Transesterification of DMC with GLY

The transesterification of DMC with GLY was carried out in a 50 ml round bottom flask equipped with a reflux condenser under vigorous stirring. In a typical run, 0.2173 mmol (1 mol %) of catalyst with respect to GLY was charged to the 50 ml round bottom flask containing GLY (2 g, 21.73 mmol) and DMC (5.87 g, 65.19 mmol). The reaction was carried out at reflux temperature by keeping the oil bath temperature at 100 °C for the selected reaction time. During the course of the reaction temperature decreased from 88 to 71 °C as the reaction progressed. The drop in temperature was because of the formation of methanol as the reaction progressed. Standard reaction was

carried out for 30 min. The reaction mixture was cooled and it was diluted with *N,N*-dimethylformamide, and a sample was taken out for analysis. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0 m \times 0.53 mm \times 1.00 μm film thicknesses). Identification of products was carried out using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer.

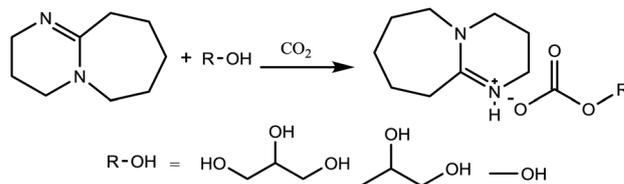
Results and discussion

Catalyst characterization

The typical reaction scheme for the preparation of the ionic liquids is as shown in Scheme 1. Based on the literature reports⁹ and also weight gain, ionic liquid formation based on methanol was quantitative, while with propylene glycol and GLY mostly the monocarbonate ionic liquid is formed. The typical ^{13}C and ^1H NMR spectra of all the ionic liquids and a physical mixture of GLY and DBU (GLY-DBU, for comparison with NMR spectrum of IL3) is shown in Fig. 1a and b, ESI,[†] and the IR spectra of ionic liquids are shown in Fig. 1c, ESI.[†] The ^{13}C -NMR spectrum of the GLY-DBU mixture showed a peak at $\delta = 162.1$, which can be attributed to the central C=N group of [DBU]. With bubbling of CO_2 into the GLY-DBU mixture, the free flowing mixture became viscous, which is a fundamental property of ILs, indicating the formation of an ionic liquid.

As reported by Anugwom *et al.*,⁸ one new peak was observed at $\delta = 159.2$ just before the peak of the central C=N group of [DBU] in ^{13}C -NMR analysis of IL3, along with all other peaks; this new peak could be because of the carbonate carbon of the ionic liquid. Similarly, peaks due to carbonate carbon are also seen at $\delta = 163.7$ and 160.8 for IL1 and IL2 (see Fig. 1a, ESI[†]). ^1H -NMR signals of the GLY-DBU mixture and IL3 showed broad and complex patterns, as reported by Anugwom *et al.*⁸ and hence assignment of signals to respective protons is difficult.⁸ Similarly the ^1H NMR for IL1 and IL2 were broad and complex and assignment of protons is difficult (see Fig. 1b, ESI[†]).

The FTIR spectra of all ionic liquids give a broad spectral response at $\sim 3400\text{ cm}^{-1}$ due to N-H stretching vibrations. The bands at 2931 and 2861 cm^{-1} were from the C-H stretching vibrations in the ring and from the alcohol. The strong band at 1650 cm^{-1} , which is comparable to the ν (C=N) group of the DBU ring, and a band at 1630 cm^{-1} can be assigned to the ν (COO⁻) group of the ionic liquid. And bands at 1324 cm^{-1} and 1106 cm^{-1} can be due to the asymmetric and symmetric C-O-C stretching vibrations (see Fig. 1c, ESI[†]).



Scheme 1 Preparation of ionic liquids.

Thus, from the IR and ^{13}C NMR analysis it can be said that the presence of peaks at $\delta = 160.8$, 163.9 and 159.2 for IL1-3 in the ^{13}C -NMR spectrum and a band at $\nu = 1630\text{ cm}^{-1}$ in IR analysis confirms the presence of the COO^- group and the formation of ionic liquids.

Catalyst screening

The ionic liquids prepared were screened for the reaction with a 30 minute reaction time using 2.5 wt% catalyst loading and the results obtained are presented in Table 1.

From the results it can be seen that all the ionic liquids prepared were active for the reaction and the best results (96% conversion of GLY with 82% selectivity to GC and 18% selectivity to GD) were obtained with IL1 at 2.5 wt% loading. GLY conversion with IL2 and IL3 prepared using propylene glycol and GLY was marginally lower with very high selectivity to GC (90 and 92%, respectively). Since higher GLY conversion with good selectivity to GC (82%) was obtained with IL1, further work was carried out using IL1 as a catalyst.

Optimization of reaction conditions

The effect of reaction parameters such as catalyst amount, reaction time, temperature, and GLY to DMC molar ratio on the activity and selectivity were investigated using IL1 as catalyst and the details are presented below.

The effect of catalyst loading on the activity and selectivity was investigated in the range of 0.01–0.66 mmol and the results are shown in Table 2.

From the results it can be seen that GLY conversion as well as selectivity pattern is significantly affected by a change in catalyst loading. The GLY conversion increased from 53% to 96% and selectivity to GC decreased from 97% to 82% with the increase in catalyst loading from 0.01–0.22 mmol. With further increase in catalyst loading, GLY conversion was not significantly affected. However, selectivity to GD increased significantly with an increase in catalyst loading (see Table 2). The probable reason for the increase in GD selectivity could be mainly because of an increase in basic sites with an increase in catalyst loading, resulting in decarboxylation of GC formed as a product. Formation of CO_2 in these experiments was confirmed by passing the gas phase through a saturated barium hydroxide solution to obtain a white precipitate of barium carbonate. Decarboxylation of the GC to GD is well known in the presence of strong bases.⁷

Table 1 Screening of various ionic liquids^a

Catalyst	GLY conversion (%)	GD selectivity (%)	GC selectivity (%)
IL1	96	18	82
IL2	87	10	90
IL3	85	8	92

^a Reaction conditions: GLY: 21.73 mmol; DMC: 65.19 mmol; catalyst: 50 mg (2.5 wt%); time: 30 minute; oil bath temperature: 100 °C.

Table 2 Effect of catalyst loading on activity and selectivity^a

Catalyst loading (mmol)	GLY conversion (%)	GD selectivity (%)	GC selectivity (%)	TON
0.01	53	3	97	1152
0.03	63	4	96	456
0.05	66	11	89	286
0.11	87	18	82	171
0.22	96	18	82	96
0.44	97	39	61	48
0.66	92	56	44	30

^a Reaction conditions: GLY: 21.73 mmol; DMC: 65.19 mmol; time: 30 minute; oil bath temperature: 100 °C. TON: number of moles of GLY consumed/no of moles of GLY charged.

The typical reaction progress and variations in conversion and selectivity pattern as a function of time using IL1 as catalyst is shown in Fig. 1. From the figure it can be seen that activity of the catalyst is high and ~89% GLY conversion is achieved with a 20 minute reaction time, with 86% and 14% selectivity to GC and GD, respectively. Conversion increased to 96% after 30 minutes' reaction time. Also, it is observed that with progress of the reaction GD selectivity increases marginally from 14 to 18% and GC selectivity decreases marginally from 86 to 82% (Fig. 1). Thus 96% conversion of GLY was obtained with 82% GC and 18% GD selectivity after only 30 minutes' reaction time.

The reaction of DMC and GLY catalyzed by IL 1 was investigated at three different temperatures (50 °C, 75 °C and 100 °C) keeping other parameters constant and the results are presented in Fig. 2. The conversion increased marginally with an increase in temperature from 50 °C to 75 °C. Selectivity to GC was very high (~95%) at 50 °C and 75 °C. However, with a further increase in temperature very high GLY conversion 96% was achieved with a marginal drop in GC selectivity (82%) and increase in GD selectivity (18%) at 100 °C (oil bath temperature). Cho *et al.*¹⁰ have observed a similar trend in the transesterification of GLY to GC using tetraalkylammonium salts immobilized on MCM-41 as the catalyst. Since very high

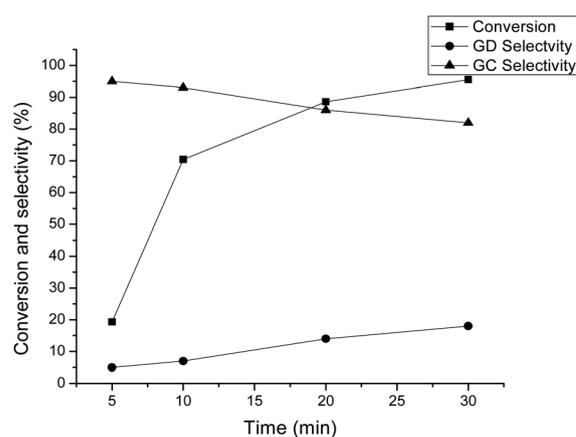


Fig. 1 Effect of reaction time. Reaction conditions: GLY: 21.73 mmol; DMC: 65.19 mmol, catalyst: 1 mol%, oil bath temperature: 100 °C.

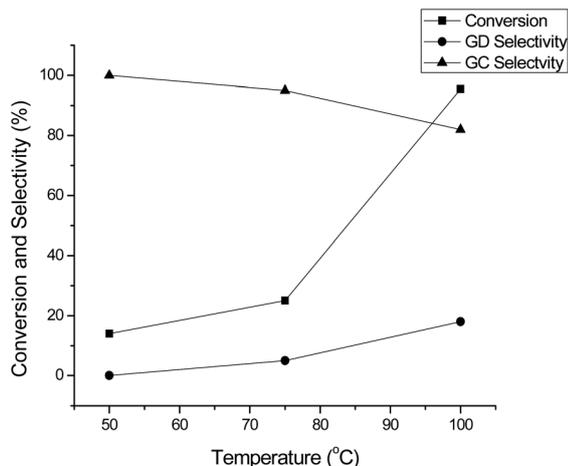


Fig. 2 Effect of reaction temperature. Reaction conditions: GLY: 21.73 mmol; DMC: 65.19 mmol, catalyst: 1 mol%, time: 30 minutes.

conversion of GLY was obtained at 100 °C, for further study the reaction temperature was fixed at 100 °C.

The effect of the GLY : DMC mole ratio on the GLY conversion and selectivity was studied by varying the GLY : DMC molar ratio in the range of 1 : 3, 1 : 2, 1 : 1, 2 : 1, and 3 : 1 and the results are presented in Table 3. A GLY or DMC quantity of 21.73 mmol was used in the experiment carried out with a GLY : DMC ratio of 1 : 1. In other experiments, the quantity of one of the reactant was varied, keeping the quantity of other reactant constant at 21.73 mmol. Also, conversion reported is based on the limiting reactant. From the results it was observed that conversion was very low (62% GLY conversion after 30 minute reaction time) at the GLY : DMC ratio of 1 : 1.

This is expected since this is an equilibrium controlled reaction and excess DMC is used to achieve high conversion.^{5,11} With increase in either GLY or DMC, conversion increased significantly, indicating a positive dependence on both reactants. High conversion (96%) was observed at a GLY : DMC ratio of 1 : 3 compared to only (68%) at GLY : DMC ratio of 3 : 1. The observed results may be due to an increase in viscosity of the reaction mixture at high GLY concentrations leading to mass transfer issues. The selectivity pattern was not affected significantly by a change in the GLY : DMC ratio.

The superior catalytic activity of IL1-3 (Tables 1 and 2) compared to the other conventional organic and inorganic

Table 3 Effect of GLY to DMC molar ratio on activity and selectivity pattern^a

GLY : DMC ratio	GLY conversion (%)	GD selectivity (%)	GC selectivity (%)
1 : 1	62 ^b	16	84
1 : 2	71 ^b	15	85
1 : 3	96 ^b	18	82
2 : 1	78 ^c	23	77
3 : 1	68 ^c	14	86

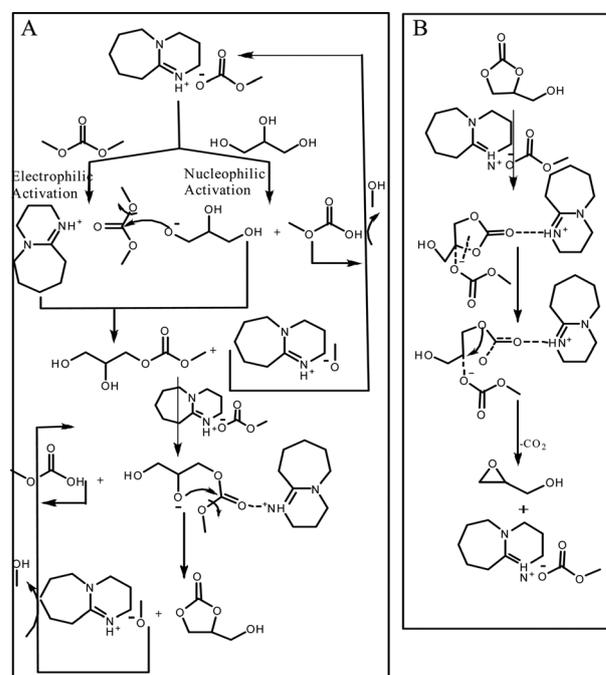
^a Reaction conditions: time: 30 minute; oil bath temperature: 100 °C, catalyst: 1 mol %. ^b Conversion w.r.t GLY. ^c Conversion w.r.t DMC.

bases³ reported in the literature has suggested that the catalytic performance of IL catalysts does not depend only on basicity. Rather, ambiphilic (both nucleophilic and electrophilic) catalysis appears more suitable to account for the results. This is based on recent proposal by Chakraborti and Roy¹² on “electrophile nucleophile dual activation” role of IL catalysts in *o*-*tert*-butoxycarbonylation of 2-naphthol with Boc₂O using 10 mol% [bmim][BF₄] as catalyst. There are a few reports on the use of IL catalysts where both anion and cation help in activation of substrates *via* ion pairs: anions and cations of ILs may activate nucleophiles (as true nucleophiles or bases) and electrophiles, respectively.^{12–14}

The role of ionic liquids IL1-3 as transesterification catalyst

Selva and co-workers¹⁵ have proposed mechanism for the synthesis of unsymmetrical carbonates involving parallel requirement of both anions and cations of IL for the activation of DMC and alcohols using methyltrioctylphosphonium salts as basic IL catalysts. Gade and co-workers⁷ in their work on direct synthesis of GD from GLY *via* GC as an intermediate have also discussed the role of both cation as well as anion in decarboxylation of GC to GD over tetramethyl ammonium hydroxide IL as catalyst.

By combining the reaction mechanism proposed by Selva *et al.* and Gade *et al.*, a plausible reaction mechanism for the transesterification of DMC with GLY to GC and decarboxylation GC to GD over IL1 is shown in Scheme 2. The nitrogen–oxygen interaction favours the coordination of the N center of IL to the basic carboxylic oxygen of DMC resulting in DMC activation. Yoshio *et al.*¹⁶ have proposed the interaction of the nitrogen



Scheme 2 Reaction mechanism: ionic liquid catalyzed [A] transesterification of DMC with GLY [B] decarboxylation of GC.

center of the quaternary ammonium salt with the carboxyl oxygen of the carboxylic acid in the reaction of ethylene carbonate with carboxylic acids to get the corresponding esters. Nucleophilic activation can take place by the proton exchange reaction between the anion of the ionic liquid and GLY leading to (GLY activation) the formation of glyceroxide and methyl carbamic acid as proposed by Selva *et al.*¹⁵ Once both the electrophile and the nucleophile are triggered by the catalyst, glyceroxide attacks the activated carbonyl carbon group, and glyceryl methyl carbonate (intermediate) is obtained. At the same time an alkoxide exchanged IL, namely $\{[\text{DBUH}^+] \text{RO}^-\}$, formed as an intermediate reacts with methyl carbamic acid formed in the first step, yielding methanol and regenerating the ionic liquid. The existence of alkoxide exchanged ILs is known in the literature.¹⁷ Methyl glyceryl carbonate undergoes a similar reaction sequence, which followed by cyclization leads to the formation of GC as the final product.

It may be noted that at very low catalyst loading (0.01 and 0.03 mmol) the selectivity to GC is very high (>95%). However, with an increase in the catalyst loading decarboxylation of GC leads to an increase in GD formation and at a catalyst loading of 0.66 mmol, 56% selectivity to GD is obtained (Table 2). An increase in IL loading will increase the interaction of IL with GC, leading to decarboxylation of GC. Gade *et al.*⁷ have proposed the interaction of cationic and anionic centres of IL with GC leading to efficient decarboxylation reaction and high (78%) selectivity to GD at higher catalyst loading in their work on the synthesis of GC/GD by the transesterification of DMC with GLY using $[\text{TMA}^+][\text{OH}^-]$ ionic liquid as catalyst. Likewise, in the present work the $[\text{DBUH}^+]$ centre can interact with the oxygen of the carbonyl group of GC, making the bond weaker. Further interaction of the anion with the more substituted sp^3 hybridized alkylene carbon of GC can lead to decarboxylation and formation of GD as the product as shown in Scheme 2. The proposed mechanism is speculative and further work is necessary to understand the mechanism of the reaction.

Conclusion

Transesterification of DMC with GLY has been investigated using DBU based ILs as catalysts. All the ILs were prepared as per the literature procedure and characterized by FT-IR and NMR analysis. Catalytic activity of all the ILs screened is very high and detailed work was carried out using IL1 as a catalyst. GLY conversion increased with an increase in catalyst loading, temperature of the reaction and also with increase in GLY or DMC concentration. Catalyst loading was found to have a significant effect on the selectivity pattern. Thus, highest selectivity (56%) to GD was achieved with a catalyst loading of 0.66 mmol. A plausible mechanism has been proposed for the

reaction. To the best of our knowledge this is the first report on the catalyst with very high activity (TON 1152) for transesterification of DMC with GLY.

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