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# 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU): A highly efficient catalyst in glycerol carbonate synthesis

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ABSTRACT

Transesterification of dimethyl carbonate (DMC) with glycerol (GLY) was investigated using various amines as catalysts. Amidines like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were found to be the best catalysts for this reaction. Best results: 98% conversion of GLY with 96% selectivity to GC (TON: 9408), were obtained with DBU as a catalyst. Effect of various reaction conditions on activity and selectivity were investigated using DBU as catalyst. The mechanism of the reaction was investigated with the help of $^{1}H$, $^{13}C$ and $^{15}N$ NMR analysis and DFT calculations.



## 1. Introduction

Glycerol (GLY) is one of the renewable resources that is produced as a waste chemical during the production of fatty acids, biofuels and biolubricants in quantities greater than the current demand. Abundant availability of GLY as a waste at low cost has drawn much attention of academia and industries for its valorization [1]. Glycerol carbonate (GC) is one of the products that can be obtained from GLY. It is a relatively new chemical in the class of cyclic carbonates, with a wide range of applications in the field of polymer, fine chemical and pharmaceutical industries. Until recently, it was produced as a specialty chemical by the stoichiometric reaction between GLY and phosgene [1]. However, because of the toxic properties of phosgene, a significant amount of work is being carried out on the development of safer routes and is still being optimized in order to compete with the conventional methodology [1]. To date, the existing state of the art confirms that the pathway based on transesterification of dimethyl carbonate (DMC) with GLY is one of the most popular routes for GC synthesis and has the potential to replace the conventional route [2]. Various kinds of organic and inorganic base catalysts [2] such as metal oxides, mixed metal oxides [3–5], hydrotalcites [6], metal complexes [7], triethyl amine [8], ionic liquids [9–11] and enzymes [12] have been used to synthesize GC by this route. However, these catalyst systems suffer from lower activity (Turnover numbers, TONs, 20–200). Therefore, the development of efficient catalysts for the conversion of GLY to GC is still a challenge. Herein, we report our results on the use of amidines as highly efficient catalysts with very high TONs for GC synthesis. In addition, the reaction mechanism is investigated in detail on the basis of $^{1}H$, $^{13}C$ and $^{15}N$ NMR spectroscopies, and density functional theory (DFT) calculations. Moreover, DFT calculations have been carried out to estimate the gas phase basicity of all the nucleophilic bases used as the catalyst.

## 2. Experimental

### 2.1. Materials

Glycerol, Glycidol, glycerol carbonate, 4-dimethylaminopyridine (DMAP), 1-*N*,*N*-dimethylpyrrole, 1,4-diazabicyclo[2.2.2]octane (DABCO), ethyl amine, butyl amine, hexyl amine, heptyl amine, octyl amine, nonyl amine, dodecyl amine, diethyl amine, triethyl amine, tributyl amine, trioctyl amine 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[5.4.0]nonene (DBN) were purchased from Sigma Aldrich. Dimethyl carbonate, dimethyl formamide and nitromethane were purchased from Spectrochem, India, and methanol was purchased from Merck, India. All the chemicals were used as received from suppliers.

### 2.2. Glycerol carbonate synthesis

The transesterification of GLY was carried out in a 50 ml round bottom flask equipped with a reflux condenser under vigorous stirring. In a typical run, 0.021 mmol (0.1 mol%) of catalyst with respect

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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 a reflux temperature by keeping the oil bath temperature at 100 °C for the selected reaction time. During the course of the reaction, the 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. The standard reaction was carried out for 0.5 h. The reaction mixture was cooled and it was diluted with *N*,*N*-dimethyl formamide, and a sample was taken out for analysis. The products were analyzed by gas chromatography on an Agilent 6890N gas chromatograph with HP-Innowax capillary column (30.0 m × 0.53 mm × 1.00 μm film thicknesses). Identification of products was done using GC–MS on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer using HP-Innowax capillary column of 30 m × 0.53 mm × 1 μm film thickness. The activity of the catalyst was based on the conversion of the limiting reagent measured under standard conditions of reaction.

### 2.3. NMR analysis

For NMR measurements, Neat sample of DBU, GLY and equimolar mixtures of DBU:GLY (DBU = 1.65 g and GLY = 0.997 g) and DBU:DMC (DBU = 1.65 g and DMC = 0.976 g) were submitted for analysis in 5 mm diameter tube. The $^{1}H$ NMR chemical shifts in parts per million (ppm) were reported with reference to $D_2O$. And $^{15}N$ NMR chemical shifts in parts per million (ppm) were reported with reference to Nitromethane. All the $^{1}H$, $^{13}C$ and $^{15}N$ spectra were recorded on a Bruker DRX 500 MHz NMR spectrometer.

## 3. Results and discussion

Spurred by recent reports, organocatalysts are now being recognized as powerful tools for GC synthesis by the transesterification of DMC with GLY [8–11]. Recently, Ochoa-Gómez et al. [8] have shown that a simple nucleophilic base, triethyl amine, is an efficient catalyst for the synthesis of GC, though high catalyst loading is required for the observed results (90–98% yield of GC at reflux temperature using 1:3 molar ratio of GLY:DMC and 10–30 mol% catalyst loading).

Keeping in mind literature reports, a range of commercially available amines were screened including, 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), for transesterification of DMC with GLY and the results are presented in Table 1. The reaction was carried out using GLY (2 g, 21.73 mmol), DMC (5.87 g, 65.19 mmol), and 0.01–2 mol% of catalyst relative to GLY. From the results obtained, it is observed that the structural variation in amines has a significant influence on its catalytic activity. Very high activity was obtained with DBU and DBN as catalysts, whereas DABCO and DMAP showed moderate catalytic activity at 0.1 mol% catalyst loading (Table 1, Entry 1, 3, 5 and 6) in only 0.5 h reaction time. Therefore, DBU and DBN were screened at a still lower catalyst concentration (0.01 mol%) with increasing reaction time and the results obtained are presented in Table 1. Best results (98% conversion of GLY with 96% selectivity to GC in 7.5 h, TON: 9408 [13]) were obtained using DBU as the catalyst (Table 1, Entry 2). To the best of our knowledge, this is the highest TON reported for the synthesis of GC. In general, all alkyl amines showed lower activity, and, hence the experiments were carried out using 2 mol% catalyst loading (w.r.t GLY) for 2 h reaction time keeping other parameters same. The activity decreased marginally with the increase in the chain length of primary alkyl amines (Table 1, Entry 8–14), while the activity increased when going from primary to secondary to the tertiary amine (Table 1, Entry 8, 15 and 16). In all the cases, the selectivity to GC was very high (83–97%). 1-*N*,*N*-dimethylpyrrole was essentially inactive for the reaction and only trace of product was observed (Table 1 Entry 7). The order of activity observed was correlated with their gas phase basicity calculated theoretically (see Supplementary information) using DFT calculations [14], and the results obtained show that the activity of amines is positively dependent on the order of basicity observed for all the amines except for DMAP (see Table 1).

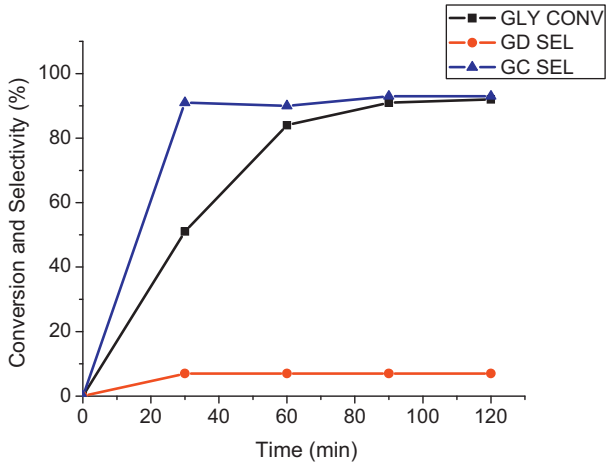



**Fig. 1.** Typical conversion time profile. Reaction conditions: GLY: (2 g, 21.73 mmol), DMC: (5.87 g, 65.19 mmol), Temp: 100 °C (oil bath temperature), Catalyst: 0.1 mol% (w.r.t GLY).

From the results, it can be seen that very high TONs of 8613 and 9408 were obtained with DBN and DBU as catalyst, respectively, in 7.5 h reaction time with high selectivity to GC (96–99%). To further confirm the effectiveness of the catalyst system, we carried out 1 mol (GLY) scale reaction with 0.01 mol% DBU (w.r.t GLY), and 88% GLY conversion with 97.7% selectivity to GC and 2.3% selectivity to glycidol (GD) was obtained in 7.5 h. This shows that comparable activity is obtained even after scaling the reaction 46 times (92 g GLY compared to 2 g GLY as reactant). We have thus demonstrated that amidines like DBU and DBN are potentially good catalysts with very high activity for the synthesis of GC. Amidines are well known organocatalysts for many reactions [15]. However, to the best of our knowledge, this is the first report on the use of amidines as catalysts for GC synthesis.

### 3.1. Effect of reaction conditions on the activity and selectivity

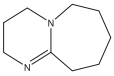
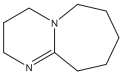
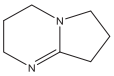
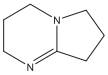
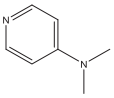
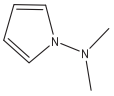
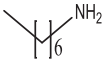
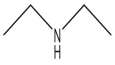
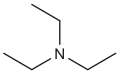
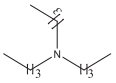
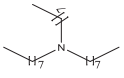
Optimization of reaction conditions was carried out using 21.73 mmol GLY, 65.19 mmol DMC and 0.1 mol% (w.r.t GLY) DBU as a catalyst and the results are presented below.

Typical conversion-time profile of the reaction is presented in Fig. 1. From the figure it can be seen that conversion increased with reaction time and reached 91% in 2 h. Selectivity to GC (90–93%) and GD (7%) was constant throughout the course of the reaction.

Effect of catalyst loading on the conversion and selectivity was investigated in a catalyst loading range of 0.1 to 0.4 mol% at a fixed reaction time of 0.5 h and the results are presented in Fig. 2.

From the results it can be seen that conversion of GLY increased with increase in catalyst loading and selectivity to GC decreased marginally with increase in selectivity to GD. The probable reason for increase in GD selectivity could be mainly because of increase in basicity of the reaction mixture with 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 saturated barium hydroxide solution

**Table 1**
Screening of catalysts for GC synthesis.

| Entry | Catalyst | Conversion (%) | Selectivity (%) | | Basicity[a] (kcal/mol) |
|---|---|---|---|---|---|
| | | | GD | GC | |
| 1[b] |  | 51 | 7 | 91 | −251.16 |
| 2[c] |  | 98 | 1 | 96 | −251.16 |
| 3[d] |  | 44 | 0 | 98 | −248.68 |
| 4[e] |  | 87 | 1 | 99 | −248.68 |
| 5[f] |  | 31 | 0 | 93 | −230.35 |
| 6[g] |  | 5 | 0 | 89 | −259.75 |
| 7 |  | T | 0 | T | −192.82 |
| 8 |  | 53 | 1 | 97 | −217.57 |
| 9 |  | 51 | 1 | 95 | −219.49 |
| 10 |  | 48 | 7 | 93 | −220.08 |
| 11 |  | 45 | 5 | 95 | −220.34 |
| 12 |  | 39 | 2 | 98 | −220.31 |
| 13 |  | 37 | 10 | 83 | −220.37 |
| 14 |  | 35 | 2 | 85 | −220.47 |
| 15 |  | 95 | 0 | 91 | −226.8 |
| 16 |  | 97 | 0 | 97 | −233.68 |
| 17 |  | 91 | 12 | 88 | – |
| 18 |  | 76 | 7 | 93 | – |

*Reaction conditions*: GLY: (2 g, 21.73 mmol), DMC: (5.87 g, 65.19 mmol), temp: 100 °C (oil bath temperature), time: 2 h, catalyst: 2 mol%.
[a] Gas phase basicity (GPB) calculated using density functional theory (DFT).
[b,d,f,g] Catalyst: 0.1 mol%, time: 0.5 h.
[c,e] Catalyst: 0.01 mol%, time: 7.5 h.

to obtain white precipitate of barium carbonate. Decarboxylation of the GC to GD is well known in presence of strong bases [10]. GLY conversion was very high for 1 h reaction time at all catalyst loadings and additional data is given in Table S1, Supplementary information.

Effect of temperature was investigated in a temperature range of 70 °C to reflux temperature (100 °C oil bath temperature) and the results are presented in Fig. 3.

Conversion of GLY increased with increase in temperature with slight drop in selectivity to GC. Thus at 70 °C, GLY conversion was 30% with 96% selectivity to GC and 4% selectivity to GD, while at reflux temperature (oil bath temperature 100 °C) GLY conversion was 91% with 93% selectivity to GC and 7% selectivity to GD.

Transesterification of DMC with GLY is an equilibrium controlled reaction and hence molar ratio of GLY:DMC used in the reaction is very important to achieve complete conversion. Effect of GLY:DMC

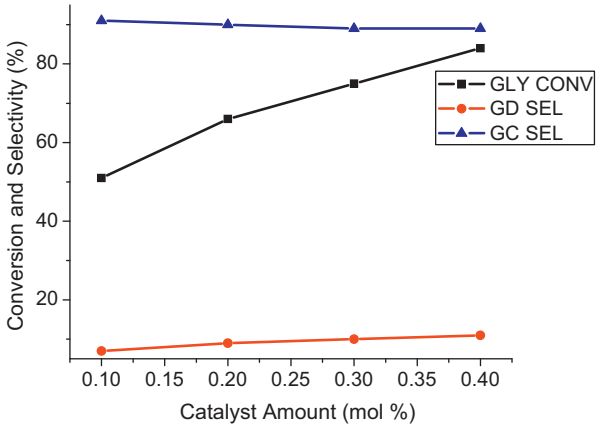



**Fig. 2.** Effect of catalyst loading. Reaction conditions: GLY: (2 g, 21.73 mmol), DMC: (5.87 g, 65.19 mmol), Temp: 100 °C (oil bath temperature), time: 0.5 h.

molar ratio was investigated in a range of 3:1 to 1:3. In this study the quantity of limiting reactant was fixed at 21.73 mmol. Thus at GLY:DMC ratio of 1:1 both reactants were used at 21.73 mmol and in other experiments the quantity of other reactant was increased accordingly. Conversion reported in this work is for the limiting reactant. The results obtained at a fixed reaction time of 1.5 h are presented in Fig. 46.

From the results it can be seen that only 70% conversion was obtained with GLY:DMC ratio of 1:1. This is expected, since this is an equilibrium controlled reaction. Selectivity to GC was 94% and GD formed by decarboxylation of GC was 6%. Conversion of the limiting reactant increased with increase in ratio indicating that the activity was dependent on both the reactants. Selectivity pattern was not affected by a change in molar ratio of GLY:DMC. Thus DBU was found to be a good catalyst with high selectivity to GC (90–96%) under the range of reaction conditions investigated. Additional data is given in Table S1, Supplementary information.

Finally recycle experiment was carried out to check stability of the catalyst. Initial experiment was carried out using 0.1 mol% catalyst loading and 1:3 molar ratio of GLY:DMC at reflux temperature for 90 min reaction time. GLY conversion of 92% was observed in this reaction with 94% selectivity to GC and 5% selectivity to GD. Required amount of fresh GLY and DMC were added to the reaction mixture to maintain GLY:DMC ratio of 1:3 and reaction was carried out again. Conversion of GLY was found to

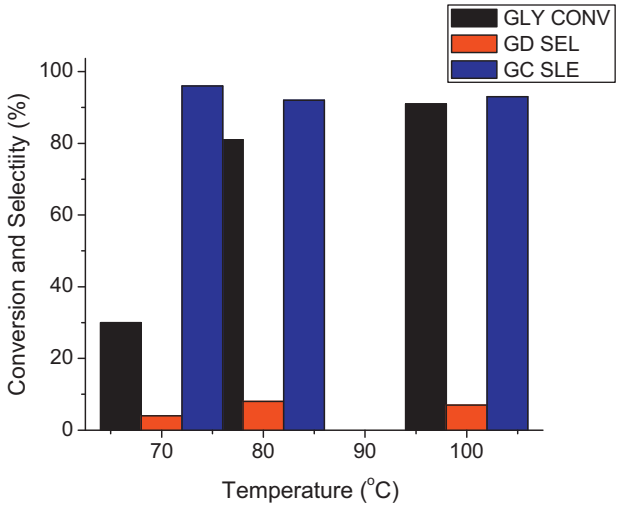



**Fig. 3.** Effect of temperature. Reaction conditions: GLY: (2 g, 21.73 mmol), DMC: (5.87 g, 65.19 mmol), time: 1.5 h, catalyst: 0.1 mol% (w.r.t GLY).

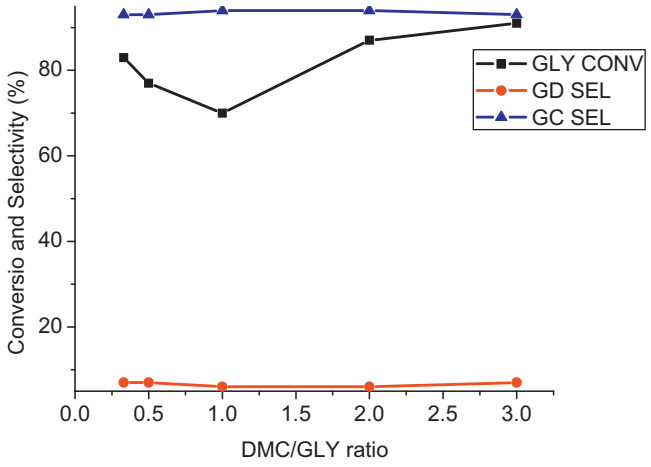



**Fig. 4.** Effect of GLY to DMC molar ratio. Reaction conditions: time: 1.5 h, catalyst: 0.1 mol% (w.r.t limiting reagent), temp.: 100 °C (oil bath temperature).

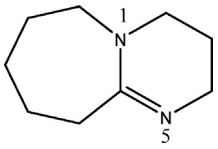



**Fig. 5.** Structure of DBU.

be lower (69% conversion for recycle experiment compared to 91% GLY conversion of run 1) during recycle of the catalyst without affecting selectivity significantly (96% selectivity to GC and 3% selectivity to GD, respectively). In this experiment significant dilution of reaction mixture is taking place and also products of the initial experiment are present in the reaction mixture. Hence activity cannot be compared with the initial experiment carried out. However, significant conversion of GLY (69%) was observed indicating that the catalyst is active in recycle experiment.

### 3.2. Mechanism of the reaction

From the GC–MS analysis, the formation of glycerol methyl carbonate (GMC) in very small quantities was observed at a low DBU loading (0.01 mol%). This indicates that GMC is formed as an intermediate and its conversion to GC is fast. The formation of GMC as an intermediate has been reported in the literature earlier [3]. However, the mechanism of GC formation from GLY has not been studied in detail and it is mentioned that the formation of glyceride from GLY by abstraction of "H" is the first step [3]. Once glyceride is formed, it attacks on the carbonyl carbon of DMC forming GMC, which further undergoes a similar reaction cycle and forms GC [3]. In order to understand the mechanistic features, we have investigated the role of DBU as a catalyst by NMR spectroscopy. For this purpose, neat samples of DBU, and equimolar mixtures of DBU:DMC and DBU:GLY were subjected to $^{15}N$ NMR analysis and the results obtained are presented in Table 2. In the $^{15}N$ NMR spectrum of free base (DBU); we observed two signals at about

**Table 2**
$^{15}N$ NMR data of DBU and equimolar mixture of DBU:DMC and DBU:GLY.

| Nuclei | DBU | DBU–DMC | DBU–GLY |
|---|---|---|---|
| N1 | −293.27 | −292.26 | −286.36 |
| N5 | −170.33 | −173.92 | −192.60 |

*Note*: [1] Chemical shifts are relative to external neat nitromethane. [2] All the three analysis were carried out without solvent, inorder to avoid complexity in interaction due to solvent.

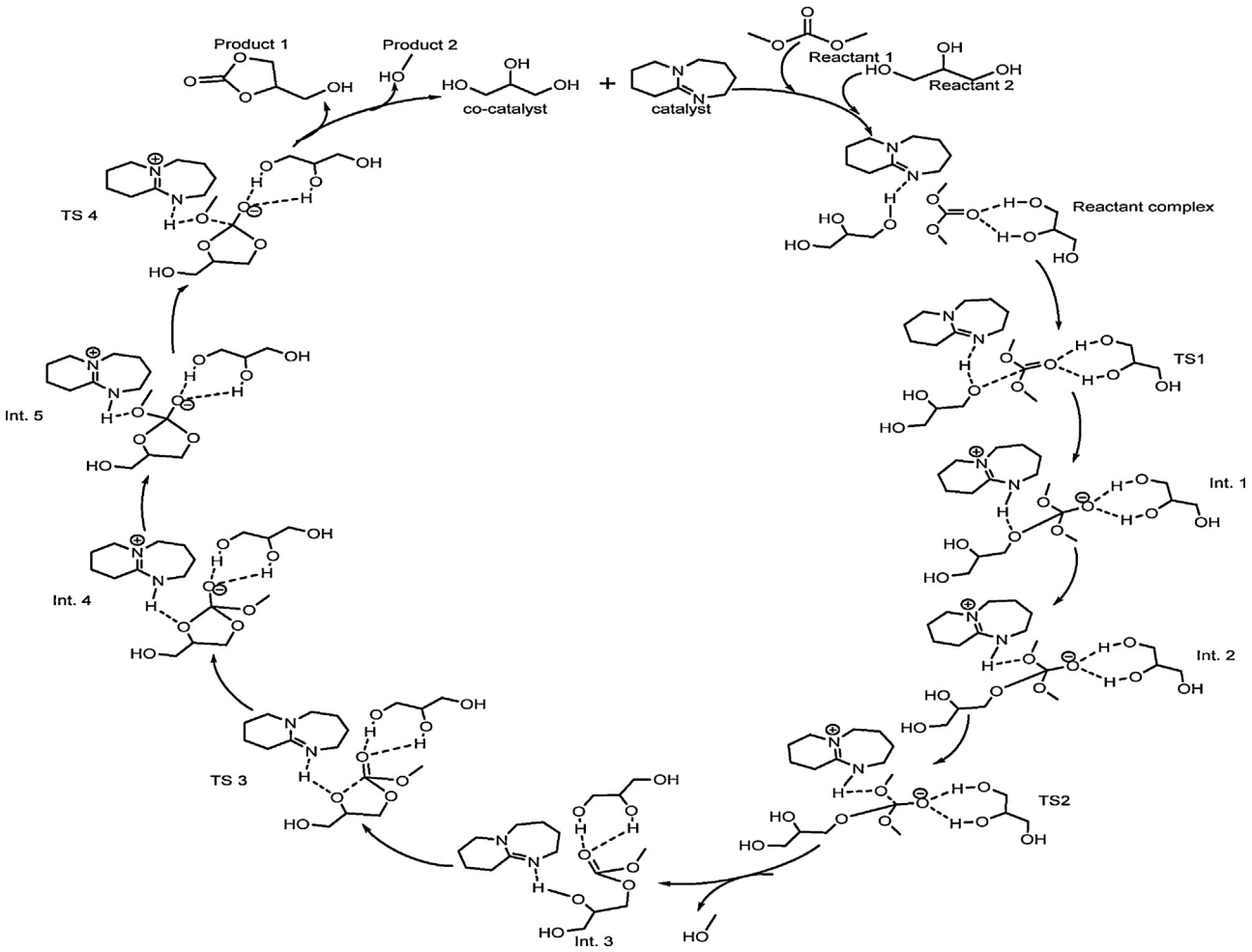



**Fig. 6.** The proposed mechanism for transesterification of DMC with GLY for GC synthesis.

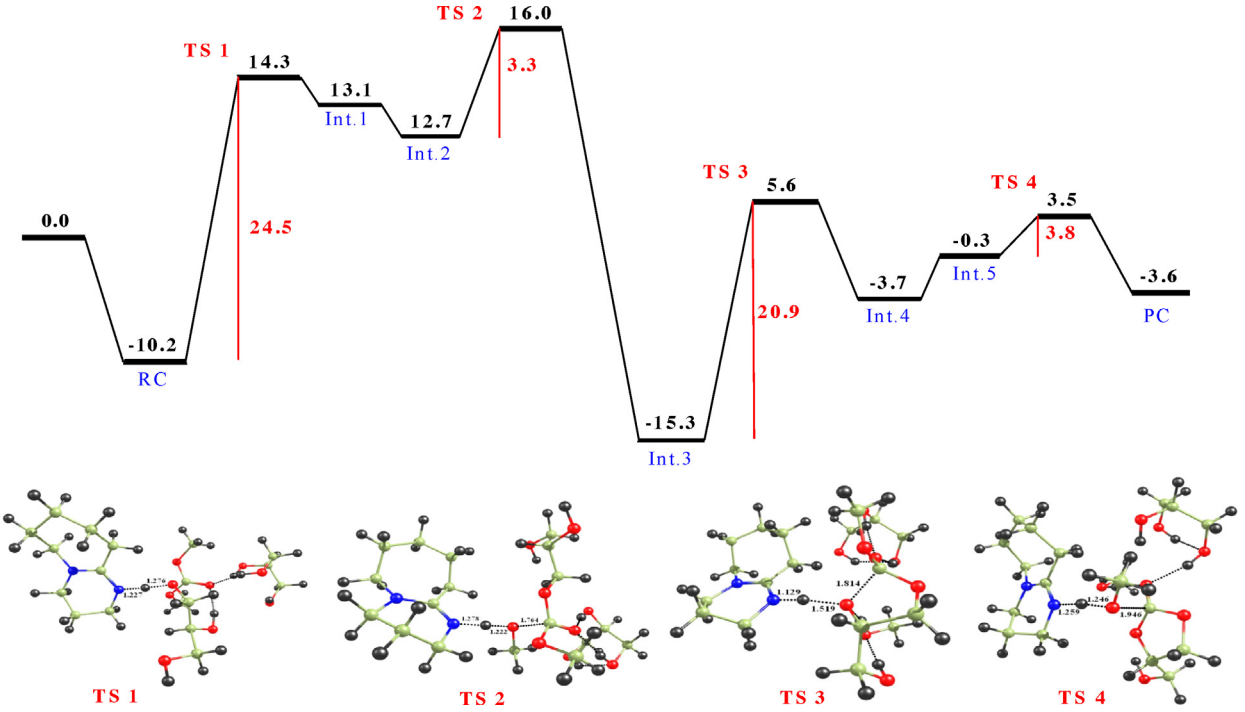



**Fig. 7.** The calculated energy diagram for the reaction of DMC with GLY to GC catalyzed by [DBU] (energies and lengths in kcal/mol and Å, respectively); green, red, black and blue balls represent carbon, oxygen, hydrogen and nitrogen, atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

−293.27 ppm and −170.33 ppm. From the literature [16] it is know that the amino nitrogen nucleus should be more shielded than the imino nitrogen by about 100 ppm. Thus we can assign these two signals to the N1 and N5 nuclei, respectively (Fig. 5).

From the results obtained it can be clearly seen that DBU:DMC mixture did not show significant changes in chemical shifts of nitrogen centers in DBU compared to the chemical shifts of nitrogen centres of DBU alone. Thus indicating that there is no interaction between electrophilic carbonyl carbon of DMC and nucleophilic nitrogen center of DBU. On the other hand, In $^{15}N$ NMR spectrum of DBU:GLY mixture it was observed that the signal for N5 nucleus shifted from −170.33 for only DBU to −192.60 for DBU:GLY mixture indicating more shielding while the signal for N1 shifted from −292.27 to −286.36 indicating deshielding (see Table 2). Similar trend of shielding and deshielding in N1 and N5 nuclei of DBU was observed by the Wiench et al. [16] in their work on detailed study of DBU and DBN protonation by trifluro acetic acid (TFA) by NMR spectroscopy. Observed NMR analysis clearly shows strong interaction between DBU and GLY.

Similarly the $^{1}H$, $^{13}C$ NMR analysis for DBU:DMC mixture did not show significant changes in chemical shifts (see spectra in Supplementary information for details), indicating that there is no interaction between DBU and DMC at room temperature. On the other hand, from the $^{1}H$ NMR spectrum of DBU:GLY mixture it was observed that all of the $^{1}H$ nuclei of GLY showed downfield chemical shift compare to the $^{1}H$ nuclei of pure GLY. All of the $^{1}H$ nuclei of DBU showed upfield chemical shift compared to $^{1}H$ nuclei of pure DBU (see Supplementary information). Thus NMR ($^{1}H$, $^{13}C$ and $^{15}N$) clearly showed that there is interaction between acidic —OH protons of GLY and "N5" nitrogen center of DBU and activation of GLY is the first step of the reaction. Thus from $^{1}H$, $^{13}C$ and $^{15}N$ NMR analysis of DBU and equimolar mixture DBU with GLY and DMC it is confirmed that the activation of GLY can takes place by the base (DBU) as a first step of this reaction.

To investigate the reaction mechanism in more detail, we have carried out DFT calculations using the Turbomole 6.4 software [17], with the TZVP/PBE/B3LYP approach [18–20]. For this purpose catalytic cycle was drawn based on the available literature and results obtained (Fig. 6). Transesterification is an equilibrium controlled reaction and, generally, one of the reactants is used in excess. Horn et al. [21] have proposed the use of an additional molecule of alcohol or amine as a co-catalyst in their work on the mechanism of DBU catalyzed amidation and transesterification of aromatic esters as a model for depolymerisation of polyethylene terphthalate. In the present work, transesterification of DMC has been carried out using GLY as alcohol and very high activity has been obtained using DBU as the catalyst. It is quite likely that an additional molecule of glycerol works as a co-catalyst and helps in stabilizing the key intermediates and transition states. The energies of reaction steps were calculated according to catalytic cycle proposed, and the results are summarized in Fig. 7. The mechanism for the conversion of GLY and DMC to the intermediate species GMC shown as "int.3" in Fig. 6 has been extensively proposed earlier by many researchers [2–4]. This essentially involves the transfer of a proton ($H^+$) from one of the GLY molecules to the nitrogen of the base DBU, followed by the transfer of the proton from the base to one of the methoxide groups to form methanol. This process goes through two transition states, having barriers of 24.5 kcal/mol and 3.3 kcal/mol (see Fig. 7). Subsequent to the formation of int.3, another OH group (sec. hydroxyl group) of the GLY moiety in GMC can undergo a similar transformation, losing a proton to the nitrogen of the base and forming a cyclic species GC, while the proton is then transferred to the remaining methoxide to provide the second methanol molecule, and yield the experimentally observed product GC. The transition states for these two base-mediated transformations have barriers of 20.9 kcal/mol and 3.8 kcal/mol, respectively (see Fig. 7). The calculations therefore indicate that the first step, corresponding to the conversion of the reactants to int.3 is the slowest step of the entire cycle, having a barrier of 24.5 kcal/mol. The role of the additional GLY molecule is also shown to be that of a stabilizing agent, *via* inter-molecular hydrogen bonding to the oxygen of the carbonyl group of DMC [21].

## 4. Conclusions

In summary, DBU was found to be the best catalyst for transesterification of DMC with GLY. $^{1}H$, $^{13}C$ and $^{15}N$ NMR analysis clearly showed strong interaction between GLY and DBU. The mechanism of the reaction was investigated with the help of DFT calculations and an additional GLY molecule was found to be involved as a co-catalyst and was also found to help in stabilizing the key intermediates and transition states. Best results: 98% conversion of GLY with 96% selectivity to GC (TON: 9408), were obtained with DBU as a catalyst (0.01 mol% based on GLY) at 100 °C in 7.5 h. To the best of our knowledge, this is the highest activity reported for the transesterification of DMC with GLY.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.04.016.

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