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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).

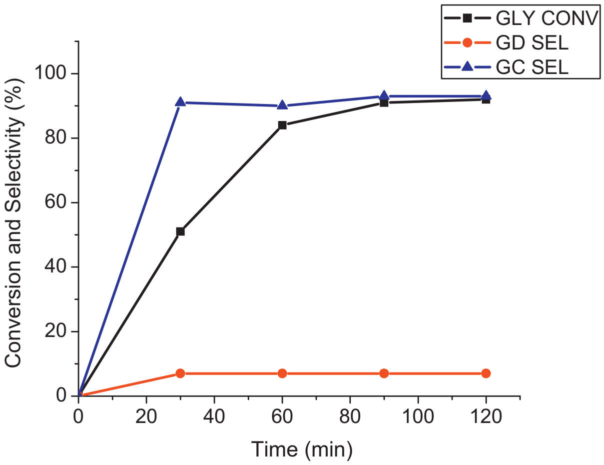

Fig. 1. Typical conversion time profile. Reaction conditions: GLY: (2 g, 21.73 mmol), DMC: (5.87 g, 65.19 mmol), Temp: 100 °C (oil bath temperature), Catalyst: 0.1 mol% (w.r.t GLY).

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