Effect of liophilicity of catalyst in cyclic carbonate formation by transesterification of polyhydric alcohols

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Received 19th February 2009, Accepted 22nd April 2009
First published as an Advance Article on the web 13th May 2009
DOI: 10.1039/b903529j

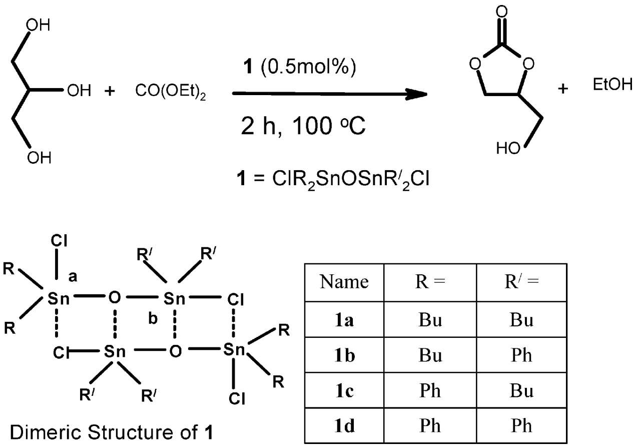
The effect of catalyst liophilicity is shown in cyclic carbonate formation by transesterification. 1,3-Dichlorodistannoxanes as liophilic transesterification catalysts facilitated cyclic carbonate formation from corresponding 1,2-diols and diethyl carbonate in continuous fashion without isolation of catalyst. Thus 0.5 mol% of catalyst could produce 1,2-glycerol carbonate quantitatively in 2 h with multiple recyclability. The product formed during the reaction was almost quantitative and did not require further purification. Isolation of catalyst at any stage showed retention of its activity and identity.

Introduction

Cyclic carbonate has many applications *e.g.* as an inert solvent or as a reactive intermediate additive.[1] In recent years, production of glycerol (GL) has increased dramatically due to growing interests in biodiesel production. As glycerol has become an inexpensive chemical, there is a great opportunity and urgency to utilize glycerol to synthesize new commodity chemicals.[2–5] Such a pressing need for GL utilization inspired us to study its transformations into new commodity materials that substantially consume GL. Glycerol carbonate (GC), which can be synthesized from GL, offers an opportunity of a renewable synthon for further chemical synthesis.[6] GC has numerous applications as a bulk or fine chemical. Nonisocyanatepolyurethane (NIPU) synthesis, developing polymer foams, solvents for cosmetics, and synthesizing biomaterials are a few recent advanced applications of GC.[7] But preparation of such a molecule has not been studied in depth and thus still offers a great challenge in making it on a commercial scale.

The use of toxic phosgene in making GC is certainly not a suitable process in terms of sustainable development. Aresta and co-workers recently reported a stoichimetric production of GC using carbon dioxide and glycerol.[8] We too have studied direct insertion of CO_2 into GL that produces GC with 35% yield catalytically.[9] However, these processes also do not seem to be commercially viable unless significant developments to increase yield are made. Transesterification of ethylene carbonate in $scCO_2$ to produce GC using a heterogeneous catalyst gives very poor yields along with several shortcomings associated with the process.[10] Diethyl carbonate (DEC), on the other hand, in presence of K_2CO_3 as transesterification catalyst can produce GC that shows commercial recognition.[11] In this method, almost quantitative yield is obtained using 3 mol% K_2CO_3 in 4 h with a turn over frequency (TOF) of ~10 h^{-1}. Nevertheless, undesired oligomers formation, formation of higher carbonated products and purification need extra care. Moreover, temperature and DEC to catalyst ratio are sensitive to making undesired products, and so purification by distillation is less preferred.[12–13]

We have found that 1,3-dichlorodistannoxanes (**1**), robustly recyclable and highly efficient (TOF, 100 h^{-1}), and several recyclable transesterification catalysts can be used for making GC from DEC and GL without using any additional solvent (Scheme 1). Convenient separation of product and a cheap catalyst are the added benefit of the process. Other carbonates, ethylene carbonate (EC) and 1,2-propylene carbonate (PC) from respective polyols, ethylene glycol (EG) and 1,2-propylene glycol (PG), showed similar efficiencies. This finding will contribute significantly to GC synthesis research with great commercial promise.



Name	R =	R/ =
1a	Bu	Bu
1b	Bu	Ph
1c	Ph	Bu
1d	Ph	Ph

Scheme 1 Transesterification of glycerol with diethyl carbonate using 1,3-dichlorodistannoxane.

Previously, **1** as transesterification catalysts has been explored in various chemical transformations and found to be a highly

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efficient catalyst compared to other conventional transesterification catalysts.[14–21] Due to high liophilicity,[22] structural rigidity and multi active catalytic centers (Sn^a, Sn^b, Scheme 1), **1** offer several advantages over alkali or other transesterification catalysts.[23,24] Fortunately, the study of **1** in cyclic carbonate synthesis has never been explored before and thus provides a great opportunity for us to explore further, especially for GC.

Results and discussion

Results indicate that almost 100% yield is obtained within 2 h using 0.5 mol% catalyst (**1a**) while maintaining a concentration of DEC and GL of 5:1. The catalysts and product can be separated easily by simple solvent extraction, which offers great advantages. Interestingly, the reaction can be continued further in the same reaction vessel after separation of product that phases out at the bottom of the reaction mixture just by adding reactants again without isolating the catalyst. This indicates that the process can be modified to a continuous one which is highly economical. We have used a series of dichlorostannoxanes catalysts to show varying reactivity patterns. EG and PG also show similar efficiency (TOF 100 h^{-1}) with **1a** (Table 1). However, separation of components from the mixture is different as described above for GL. There is no phase separation in the case of EG and PG upon addition of hexane.

All the catalysts, **1a**[25], **1b**[25], **1c**[26] and **1d**[27] are synthesized in a single reaction step from a cheap readily available source of materials according to previously reported literature procedures. ^{1}H-NMR, electrospray ionization mass analysis and elemental analysis data are in complete agreement with reported values.

Typically, DEC and GL forms two phases, is placed in a round bottom flask and 0.5 mol% catalyst (with respect to GL) is added to the reaction mixture. The catalyst is completely miscible in the reaction mixture. The mixture becomes a single phase upon heating, which remains like that throughout the reaction and even after cooling. After completion, addition of hexane to the reaction mixture at room temperature forms two layers. The bottom layer is GC, which can be separated out easily. On the other hand, excess DEC, catalyst and hexane form the top layer. Evaporation of the top layer yields catalyst and excess DEC. 98% Hexane can be recovered from the top layer and further recycled. Ethanol forms during the reaction by the expanse of DEC, mostly remaining in the upper phase. Addition of GL and DEC (to maintain the initial ratio) to the mixture of recovered catalysts and DEC can initiate the GC synthesis again. We have performed 5 such reaction cycles in this manner and found out that there is no depletion in productivity (Table 2). Therefore, it is possible to run the reaction in a continuous fashion as shown in Fig. 1.

Table 1 Reactivity of **1a** with different polyols

Reactants	Products	Time/h	Catalyst	Yield/%
GL	GC	2	**1a**	99.1
PG	PC	2	**1a**	99.4
EG	EC	2	**1a**	99.0

Reaction conditions: Substrate 0.87 mol, Cat 4.3 mmol, DEC 4.35 mol, 100 °C, yield by gas chromatography column DB-5 FID.

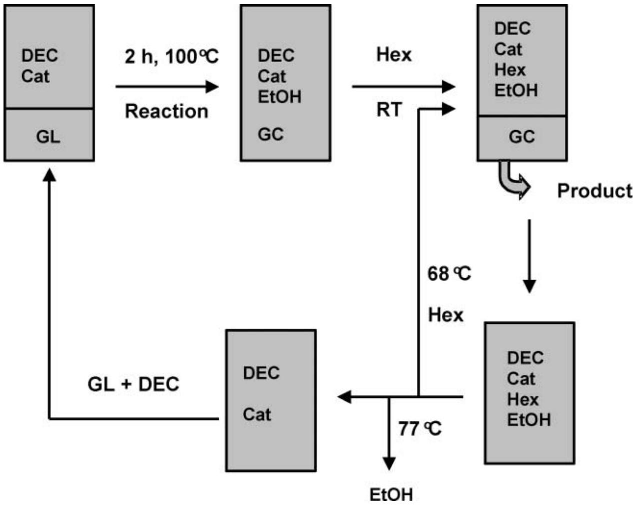

Fig. 1 Schematic representation of glycerol carbonate synthesis in a continuous manner. DEC = diethyl carbonate, Cat = Catalyst, GL = glycerol, Hex = hexane, RT = room temperature, EtOH = ethanol.

The catalyst can also be recovered by distilling off DEC after removal of hexane. We have recovered up to 98% of the catalyst and verified the recovery process by 5 independent studies. 2% loss is most likely due to manoeuvre error. The recovered catalyst

Table 2 Recyclability test of catalyst **1a** for GC formation

						Isolated amount	
Cycle		GL/g	DEC/g	**1a**/g	Hex[d]/mL	[e]GC/g	[f]EtOH/g
1	U[a]	80	514	2.4	500		
	R[b]		411		480	102	70
2	U	[c]+ 80	+ 103		+ 20		
	R		410		480	102	70
3	U	+ 80	+ 104		+ 20		
	R		411		480	102	70
4	U	+ 80	+ 103		+ 20		
	R		410.5		490	102	70
5	U	+ 80	+ 103		+ 0		
	R		410	2.35	490	101	70

[a] U = Used amount. [b] R = Recovered amount. [c] + indicates the amount added to the recovered component from the last cycle. [d] Hex = hexane. [e] Isolated amount. [f] Ethanol produced was measured from the hexane layer. Temp. 100 °C, reaction time in each cycle 2 h.

is found to be same as the starting one, which can be confirmed by identical elemental (C, H) analysis, mass spectrometer and ^{1}H NMR. This is one of the biggest advantages of using chloro distannoxane over alkoxy distannoxane for transesterification reaction as the later transforms into a different composition after the reaction.[28] This gives a great opportunity to recycle **1**.

The progress of the reaction was monitored by gas chromatography using a DB5 column. The yield was estimated by an external standard method using authentic GC. GC formation using **1a** continues to completion within 2 h as revealed by gas chromatography studies (Fig. 2). Formation of GC was confirmed by the characteristics of a FTIR carbonyl signal (>C=O) as an infra red peak[11] at 1788 cm^{-1}, ^{13}C NMR peak at 157.8 ppm[29] and molecular ion mass peak at *m*/*z* 117.

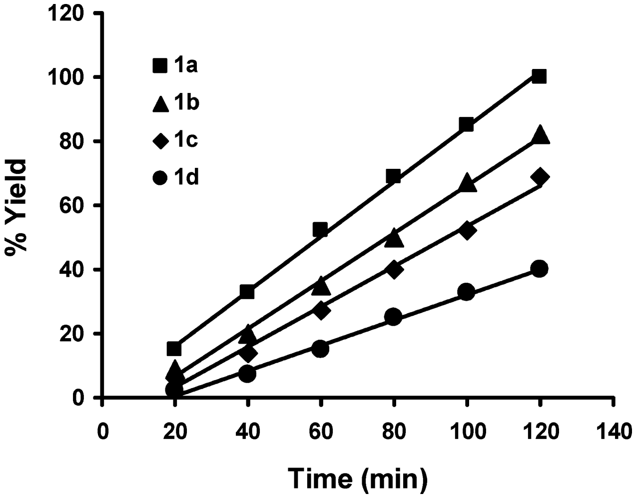

Fig. 2 Efficiencies of different catalysts on glycerol carbonate formation. Reaction conditions: GL 0.87 mol, Cat 4.3 mmol, DEC 4.35 mol, 100 °C, yield using a DB-5 FID gas chromatography column.

The observed high TOF of 100 h^{-1} of **1a** can be attributed to the following reasons: a) a high degree of homogeneity arising due to the liophilic nature[30–31] of **1**, which makes the catalyst perform efficiently compared to the heterogeneous catalytic system and b) the dimeric nature of **1**[32] with two different Sn centers (Sn^a, Sn^b, Scheme 1) which have a different Lewis acidity[33] and thus are able to activate both ester and alcohol simultaneously to form products making the catalysts more efficient than a conventional one.

The liophilic nature of the catalyst facilitates its dissolution in hexane and thereby separation from the product. Liophilicity increases upon esterification of alcohol[34] and thus the order for GL follows GL < GC < DEC < **1a**. The significant difference in polarity due to the presence of –OH in GC from hexane and DEC facilitates the catalyst extraction through hexane leaving glycerol carbonate in a separate phase. This makes the process advantageous for GC compared to EC and PC, which remain in a single phase making separation difficult. Due to the smaller polarity difference of EC or PC with hexane or DEC no phase separation occurs. This is supported by the observation that **1d**, practically insoluble in hexane, sets at the bottom on addition of hexane.

We have studied ICP-OES and ion chromatography analyses for tin and chlorine respectively, of the product and found no tin or chlorine (if leached from the catalyst) residues present in the product. It is apparent from Fig. 2 that introducing phenyl groups in the catalysts reduces activity significantly from its butyl analogue. The structural dissymmetry in **1b** and **1c** is also spectacularly reflected in the activity differences of the catalysts. However, it is of further interest to attempt to detail kinetic and mechanistic studies that will explain these observations.

Conclusions

In conclusion, we have shown that catalyst liophilicity can accelerate reaction rate tremendously and provides the benefit of easy separation of components from the reaction mixture as well. **1** is found to act as a recyclable catalyst, which can form glycerol carbonate from diethyl carbonate and glycerol very efficiently with the additional benefits of easy product separation. Thus the procedure provides a completely continuous method of making glycerol carbonate without the requirement of separating catalyst and thus overall the process is highly economical and environmentally friendly.

Experimental

General

Chemicals were purchased from Aldrich chemical company, USA and used without further purifications unless otherwise mentioned. Solvents were purified using standard purification procedures before using in any reactions. Chloride was estimated using an Ion Chromatography (Metrohm) method. Tin was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer, Optima 4300 DV) within the limit of 1 ppm. Reaction products were analyzed by Gas Chromatography (Shimadzu, GC 2010) using a DB-5 column (J & W Scientific). ^{1}H-NMR spectra were obtained in a 300 MHz Varian FT spectrometer using deuteretated solvent as the lock. The spectra were collected at 25 °C and chemical shifts (δ, ppm) were referenced to residual solvent peak ($CDCl_3$ δ, 1H, 7.26 ppm). Electrospray ionization mass spectra (ESI-MS) were recorded using a Micromass Q-TOF mass spectrometer. Infra Red (IR) spectra were recorded using a Perkin Elmer, Spectrum 100 instrument. The elemental analyses (C, H) were carried out with a Perkin-Elmer 240 C elemental analyzer.

Method of transesterification

513.86 g (4.35 mol) of DEC, 80.0 g (0.87 mol) GL and 2.40 g (0.0043 mol) catalyst **1a** were placed in a three necked round bottom flask and heated at 100 °C for 2 h. The initial biphasic solution containing GL at the bottom and catalyst dissolved in DEC on top became an homogeneous solution within 10 min. The progress of the reaction was monitored with a Shimadzu 2010 gas chromatograph using a DB 5 column comparing with authentic GC. After 2 h, the flask was cooled to room temperature. Hexane (500 mL) was added into the reaction mixture and stirred for a few mins. The bottom portion separated out as product, GC. The top layer contains **1a**, ethanol produced and excess DEC. DEC and **1a** were reused for the next reaction cycle after separation of hexane (68 °C) and ethanol (77 °C) by step wise distillation. 486 ml Hexane and 75 g ethanol were recovered. 503.6 g of DEC and 2.27 gm catalyst were retained; adding 78.0 gm of DEC and 80.0 gm of GL, the catalyst mixture was recycled. Recovered hexane was reused for the next cycle. The same procedure was followed for other catalysts.

EG and PG was used in a similar manner and purification was carried out by distillation.

Preparation of catalysts

Preparation of 1,3-dichloride-1,1–3,3-tetrabutyldistannoxane (1a). **1a** was synthesized according to published procedures.[25] A mixture of Bu_2SnO (1.0 g, 4.0 mmol) and Bu_2SnCl_2 (1.22 g, 4.0 mmol) in toluene (50 mL) was refluxed for several hours. After 10 h reflux, the reaction mixture became a clear solution. The reaction was further refluxed for another 7 h. The hot mixture was filtered and concentrated in vacuum to get 1,3-dichlorotetra-*n*-butyldistannoxane (**1a**). Pure product was obtained by recrystallizing from toluene. Yield 95%; Melting point, 110 °C (from ethanol) (lit.[25] 110 °C). Elemental analysis: Found C, 34.61; H, 6.52; Cl, 12.85; Sn, 43.01. Calculated for $C_{32}H_{72}Sn_4O_2Cl_2$: C, 34.64; H, 6.54; Cl, 12.83; Sn, 42.95. ESI-TOF mass: m/z 1106.47. ^{1}H NMR: δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.87 (12H, t, Me), 1.4 (8H, m, Sn–CH_2–), 1.8 (16H, m, CH_2–CH_2).

1b and **1c**. These catalysts were synthesized following a previously published literature method.[26]

Preparation of 1,3-dichloride-1,1-dibutyl-3,3-diphenyldistannoxane (1b). Bu_2SnO (0.720 g, 2.90 mmol) and Ph_2SnCl_2 (1.0 g, 2.908 mmol) were dissolved in 25 mL acetone in a 100 mL round bottom flask and refluxed for 3 h while stirring the reaction mixture. Most of the solid dissolved within 3 h of the reaction. After filtration, the reaction mixture was cooled at room temperature and concentrated to obtain a solid product. Pure needle shaped crystals of **1b** were obtained after crystallizing the solid from hexane. Yield 90%; Mp, 148 °C. Elemental analysis: Found C, 40.58; H, 4.54; Cl, 12.03, Sn, 40.06. Calculated for $C_{40}H_{56}Sn_4O_2Cl_2$: C, 40.52; H, 4.76; Cl, 11.96; Sn, 40.05. ESI-TOF mass: $m/z \times 2$, 1185.76 (Calculated, 1185.46). ^{1}H NMR: δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.93 (6H, t, CH_3), 1.65 (4H, m, Sn–CH_2–), 2.37 (8H, m, –CH_2–CH_2–), 7.65 (6H, m, ^{o}Ph), 8.69 (6H, m, ^{m,p}Ph).

Preparation of 1,3-dichloride-1,1-diphenyl-3,3-dibutyldistannoxane (1c). Ph_2SnO (1.0 g, 3.46 mmol) and Bu_2SnCl_2 (1.05 g, 3.45 mmol) were dissolved in 25 mL acetone in a 100 mL round bottom flask and refluxed for 5 h while stirring the reaction mixture. The reaction mixture was then cooled to room temperature and filtered to remove any insolubles. A solid product was obtained after concentrating the reaction mixture under vacuum (55 °C, 65 mmHg). Pure crystalline **1c** was obtained after crystallizing the solid from hexane. Yield 75%; Mp 152 °C (lit.[26] 149 °C). Elemental analysis: C, 40.54; H, 4.28; Cl, 12.01; Sn, 40.03. Calculated for $C_{40}H_{56}Sn_4O_2Cl_2$. C,40.52; H, 4.76; Cl,11.96; Sn, 40.05. ESI-TOF mass: $m/z \times 2$, 1185.813, (Calculated 1185.46). ^{1}H NMR: δ_H(300 MHz; $CDCl_3$; Me_4Si); 1.22 (6H, t, CH_3), 1.91 (4H, m, Sn–CH_2–), 2.77 (8H, m, –CH_2–CH_2–), 7.41 (6H, m,^{o}Ph), 8.18 (6H, m, ^{m,p}Ph).

Preparation of 1,3-dichloride-1,1,3,3-tetraphenyldistannoxane (1d). **1d** was synthesized as per the literature reported procedure.[27] Ph_2SnCl_2 (1.0 g, 2.9 mmol) and 2-aminobenzthiazole (436 mg, 2.9 mmol) in 25 mL acetone were stirred for 3 h while a white precipitate appeared during the reaction. The solution was filtered to remove any insolubles and evaporated to dryness to yield a solid white product. Yield 25%; Mp, 198 °C (lit.[16] 195 °C). Elemental analysis: C, 45.67; H, 3.37; Cl, 11.24; Sn, 37.50. Calculated for $C_{48}H_{40}Sn_4O_2Cl_2$. C,45.56; H, 3.19; Cl,11.21; Sn, 37.52. ESI-TOF mass: $m/z \times 2$, 1265.441, (calculated 1265.42). ^{1}H NMR: δ_H(300 MHz; $CDCl_3$; Me_4Si); 7.61 (8H, m, ^{o}Ph), 8.58 (12H, m, ^{m,p}Ph).

Estimation of Cl^- and Sn in the catalysts

A representative method for the estimation of % of Cl^- and Sn of catalyst **1a** is described here. This was run similarly wherever required in order to obtain the % of Cl^- and Sn: **1a** (110 mg, 0.1 mmol) was digested with an equivalent amount of concentrated HNO_3 (69%) in a porcelain crucible for 5 h. The resultant digested mass was then evaporated to dryness. The solid obtained after evaporation was dissolved in 10 mL water and acidified with dilute HNO_3 (6.9%) until the solution turned clear. After filtering the solution, the filtrate was transferred into a 100 mL volumetric flask and diluted with water. The solution was then analyzed to estimate Cl^- by using a Metrohm column in an ion chromatography method. The same solution was used to determine Sn content by ICP-OES.

Acknowledgements

We greatly acknowledge financial help from Reliance Industries Limited. We are very much thankful to Dr. A. J. Sophia, Dr. G. Kalpana, G. M. Desai and K. Solanki for analytical help.

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