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Methanol assisted selective formation of 1,2-glycerol carbonate from glycerol and carbon dioxide using ^{n}Bu$_2$SnO as a catalyst

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ABSTRACT

Selectively 1,2-glycerol carbonate was obtained from glycerol and carbon dioxide in methanol using 1 mol% ^{n}Bu$_2$SnO (dibutyltin(IV)oxide, **1**) as a catalyst. The reaction attained equilibrium in 4 h and the yield of 1,2-glycerol carbonate obtained was as high as 35%. We observed the rate of the reaction depends on the amount of the catalyst and methanol used. During the reaction we could trap the intermediates and identify it by ^{13}C NMR, IR and mass spectrum of the reaction mixture. The reaction proceeds upon activation of **1** by methanol forming dibutyltindimethoxide followed by dibutyltinglycerate, which undergoes CO$_2$ insertion to produce non-isolable 7-membered tin–glycerolcarbonato complex that finally yield glycerol carbonate. Catalyst **1** was found to be successful even with 1,2-propanediol and ethylene glycol yielding the corresponding cyclic carbonate.

1. Introduction

In addition to few of our contributions on preparation of useful chemicals from CO$_2$ in past [1–5], we took an attempt to produce glycerol carbonate from glycerol and CO$_2$. Because, surplus glycerol produced (8–10% by weight) as a by-product during biodiesel process is a serious concern [6] and hence extensive utilization is therefore a pressing need to reduce over supply of glycerol [7]. Glycerol carbonate is one of the important precursors and can also be considered as renewable synthons having numerous applications in polymer materials as well as in synthetic organic chemistry [8–10]. The synthesis of glycerol carbonate is commonly pursued in an indirect method by reacting glycerol with carbonyl sources such as phosgene, dialkyl carbonate, urea or alkylenecarbonate, etc. [11–14]. Direct carbonation of glycerol using carbon dioxide would be one of the lurking opportunities since two amply available resources could give a valuable product which makes the process at its best with 87% atom efficiency. The idea of making cyclic carbonic esters using CO$_2$ into 1,2-diol and 2-amioalcohol is already been in practice. Commercially available cheap metal oxides can from cyclic carbonate from corresponding diol according to Du et al. [15,16]. Organic super bases like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) can also from cyclic carbonate as Huang et al. reported [17]. Tomishige et al. prepared cyclic carbonate from corresponding diol using ceria-based catalyst [18]. We were inspired by these observations to extend the concept into glycerol to form glycerol carbonate.

Findings of past studies involving direct insertion of CO$_2$ into glycerol using **1** and *n*-dibutyltindimethoxide (**2**) in absence of any solvent resulted glycerol carbonate with turn over numbers (TON) 0.21 and 1.14, respectively, in 6 h at 180 °C and 5 MPa CO$_2$ pressure [8]. The author accounted the catalyst insolubility and deactivation into polymeric alkyltinoxides as the reason for its low TON.

Du's work related to propylene carbonate formation from propylene glycol and CO$_2$ using **1** showed very good catalytic activity. Author approached dehydrating condensation between **1** and propylene glycol that brings into catalytic cycle [16]. Moreover, **1** and **2** showed comparable activity in Du's experiment. What authors found that apart from solubility, removal of water was necessary to improve the yield at significant level. Thus yield of propylene carbonate moved from 2% to >30% while dehydration of diol was carried externally and separately by transforming diol into a ketal prior to condensing with CO$_2$. Similarly, enhanced yield using **1** had also been observed during condensation of 1,2-amino alcohol with CO$_2$ for making oxazolidinones [19].

These observations may be indicative for an opportunity to improve the yield of glycerol carbonate by effective dehydrative condensation of glycerol and CO$_2$ using **1** that can resolve solubility burden. We found that addition of alcoholic solvents in Aresta's reaction could accelerate the rate and so yield tremendously at

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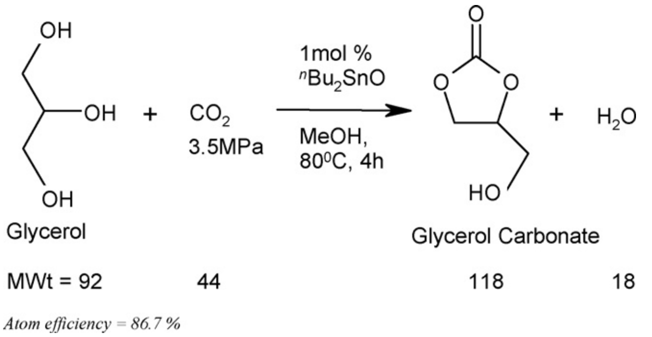


Scheme 1. Direct synthesis of glycerol carbonate.

comparatively milder condition. We did carry out the same reaction with methanol and found the yield agreeably larger, 35% in 4 h at 80 °C and 3.5 MPa CO_2 pressure using 1 mol% of **1**.

Herein we report the formation of 1,2-glycerol carbonate by direct insertion of CO_2 into glycerol using inexpensive and amply market available di(*n*-butyl)tin(IV)oxide, **1** in catalytic amounts in presence of methanol (Scheme 1). In addition we have evaluated the mechanistic pathway by identifying the intermediates spectroscopically. With best of our knowledge this is first example of glycerol carbonate formation in a truly catalytic manner from glycerol and carbon dioxide.

2. Experimental

2.1. General

The reagents handled and reactions performed were under dry and inert atmosphere throughout. Methanol, ethanol, 1-propanol, ethylene glycol, 1,2-propanediol, glycerol and 2,2-dimethoxypropane were purified using standard purification procedures [20]. Di(*n*-butyl)tin(IV)oxide (n-Bu_2SnO) **1**, di(*n*-butyl)tin(IV)dimethoxide (n-$Bu_2Sn(OMe)_2$) **2**, di(*n*-butyl)tin(IV) dichloride (n-Bu_2SnCl_2) **3**, dimethyldigol and deuterated methanol were purchased from Aldrich Chemical Co., USA and were used as received. Carbon dioxide (purity 99.99%, moisture 5 ppm, oxygen 5 ppm) was purchased from Ultra Pure Gases India Pvt. Ltd., India. 13X (soda) was obtained from EOP and used after activation at 350 °C for 3 h. Products were analyzed on Shimadzu gas chromatograph system (GC), 7AG using 6m 3% OV 17 column. Infra red (IR) spectroscopy was done on a Perkin Elmer 100 Infra red spectrometer. ThermoFinnigan mass spectrometer equipped with direct mass (MS) probe was used for GC–mass (GC–MS) analysis of glycerol carbonate. Electro spray ionization mass spectra (ESI-MS) with a Micromass Q-TOF was used for analysis of **4** and solid reaction mixture. Elemental analysis was carried on a Perkin Elmer PE 2400 (accuracy ±0.3%). Amount of tin was estimated using inductively coupled plasma optical emission spectroscopy (ICP-OES), Perkin Elmer, model 4300 DV. NMR was recorded on Varian 300 MHz using CD_3OD as locking solvent. A 100 mL Parr reactor with 4842 controller was used for high pressure reactions. The reactor was activated at 150 °C for 1 h and flashed thoroughly with nitrogen and finally with CO_2 to make it free from moisture before the reaction.

2.2. Preparation of glycerol carbonate

0.2 g (2.17 mmol) glycerol, 0.05 g (0.02 mmol) Bu_2SnO, **1** (1mol%) and 10 mL (24.7mmol) methanol were taken in a pre-activated 100 mL Parr reactor and kept stirring at 300 rpm. Carbon dioxide was then introduced into the mixture directly from cylinder at 1.8 MPa pressure at ambient temperature, which showed 3.5 MPa pressure upon heating at 80 °C. Reaction was stopped after 4 h by cooling the reactor in an ice salt mixture (−22 °C) and then depressurized slowly. Solution was filtered and the filtrate was analyzed through GC. Required quantity of 13X, wherever used, was pre-activated at 350 °C for 8 h and was introduced with catalyst and substrate. Molecular ion peak at m/z 117 in mass spectrum and a strong IR peak at 1790 cm^{-1} confirm the formation of glycerol carbonate. Progress of reaction was monitored in GC and yield was estimated by external standard method using authentic samples.

2.3. Preparation of dibutyltinglycerate, **4**

To a solution of 0.2 g (2.17 mmol) glycerol in 25 mL methanol, 0.54 g (2.17 mmol) of **1** was added and refluxed for 3 h. The reaction mixture which was heterogeneous at the start of the reaction gets transformed into homogeneous form slowly over a period of 1 h. Evaporation of methanol under reduced pressure resulted a solid mass, which upon recrystallization in hexane yield dibutyltinglycerate as white crystals. Yield 96%. Anal. Calc. for $C_{11}H_{24}O_3Sn$: C, 40.90; H, 7.49; Sn 36.75%. Found: C, 41.02; H, 7.63; Sn, 36.2. IR (KBr): 3270 cm^{-1} (s), 2956 cm^{-1} (s), 2913 cm^{-1} (s), 2856 cm^{-1} (s), 1120 cm^{-1} (m), 642 cm^{-1} (m). m.p. 150 °C and $m/z = 322$.

Preparation of **4** was also carried by refluxing 5 g (16.95 mmol) of **2** with 16 g (173 mmol) of glycerol under continuous stirring in nitrogen atmosphere for 1 h. Amount of methanol was measured by GC over period of time. The resulted solution was diluted with hot hexane and filtered at warmed condition. Excess glycerol was separated from bottom layer and hexane was removed under reduced pressure. Solid mass was recrystallized under hexane and analyzed. This showed similar results of **4** as mentioned above that prepared from **1**.

2.4. Estimation of Sn

24.9 mg (0.1 mmol) of **1** was digested with equivalent amount of concentrated HNO_3 (assay 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 then acidified with dilute HNO_3 (assay 6.9%) until the solution become clear. After filtering the solution, the filtrate was transferred into a 100 mL volumetric flask and was made up to 100 mL with distilled water. The solution was then analyzed to determine Sn content by ICP-OES.

2.5. Infra red, ^{13}C NMR and mass spectral studies of the reaction mixture

0.102 g (1.1 mmol) of glycerol, 0.049 g (0.01 mmol) of di(*n*-butyl)tin(IV)oxide, Bu_2SnO, **1** (1 mol%) and 5 mL deuterated methanol (CD_3OD) were taken in pre-activated 100 mL Parr reactor. After depressurization, the reaction mixture was quickly transferred and filled into NMR tube under positive pressure of CO_2, sealed, taken to low temperature by using into dry ice-acetone mixture and recorded the NMR without any delay. Similarly the reaction mixture was transferred into liquid infra red cell and immediately recorded the spectrum. The remaining solution was concentrated under reduced pressure at ambient temperature and the semi-solid mass separated from viscous liquid, mixture of glycerol and glycerol carbonate, was immediately taken to mass spectrometer through direct probe and recorded the spectrum.

2.6. Reaction of **4** with methanol

According to literature reported [8] modified procedure, 5 g (15.5 mmol) of **4** was taken with 16 mL (157 mmol) methanol in 25 mL toluene under nitrogen atmosphere. The mixture was

Table 1
Effect of catalyst concentration, pressure, temperature, methanol and time[a].

Entry	Catalyst	Cat. conc. (mol%)[b]	Temp. (°C)	Pressure (MPa)	Methanol (mL)	Time (h)	Yield (%)
1	**1**	0.1	80	3.5	10	4	2
2	**1**	1	80	3.5	10	4	10
3	**1**	1 + 13X 1.0 g	80	3.5	10	4	18[c]
4	**1**	1	120	3.5	10	4	22
5	**1**	1	80	13.8	10	4	25
6	**1**	1	120	13.8	10	4	30
7	**1**	1 + 13X 1.0 g	120	13.8	10	4	35[c]
8	**1**	1	80	3.5	0.004	4	0.8
9	**1**	1	80	3.5	0.017	4	10
10	**1**	1	80	3.5	10	2	2.5
11	**1**	1	80	3.5	10	4	10
12	**1**	1	80	3.5	10	4.5	11
13	**1**	1	80	3.5	0	4	0[d]
14	**1**	1	80	3.5	0.004	4	0.8[d]
15	**2**	1	80	3.5	10	4	7.7
16	**3**	1	120	6.5	10	4	0
17	**4**	1	80	3.5	10	4	0.98

[a] 0.2 g glycerol, 0.05 g catalyst, 10 mL methanol, 3.5 MPa CO_2, 4 h, 80 °C, 100 mL Parr reactor, 300 rpm were used except respective parameters that varried.

[b] Mol% was calculated with respect to glycerol 0.2 g.

[c] 13X zeolite was introduced at the beginning of reaction.

[d] Dimethyldigol (diglyme) 10 mL was used along with methanol.

refluxed for 5 h under stirring. Released glycerol was measured by GC over period of time.

2.7. *Carbonation of* ***2*** *and* ***4***

As described above in case of glycerol carbonation, 0.5 g (1.55 mmol) of **4** and 10 mL (24.7 mmol) methanol were taken in a pre-activated 100 mL Parr reactor and kept stirring at 300 rpm. Carbon dioxide was then introduced into the mixture directly from cylinder at 1.8 MPa pressure and heated at 80 °C. Reaction was stopped after 4 h by cooling the reactor in an ice salt mixture (−22 °C) and then depressurized slowly. Solution was filtered and the filtrate was analyzed through GC.

Similarly respective amount of reactants were taken for carbonation of **2**.

3. Results and discussion

3.1. *Carbonation of glycerol*

Glycerol carbonate was obtained from carbon dioxide and glycerol using 1 mol% of catalyst, **1** in presence of methanol at 80 °C and 3.5 MPa CO_2 pressure in 4 h. Progress of reactions was monitored through GC by comparing it with respective standards and the yield of the product was quantified by external standard method using authentic glycerol carbonate solution. Selected data are shown in Table 1 that represents effect of various reaction parameters. The reaction was found to be 100% selective to 1,2-glycerol carbonate as we did not observe any impurities including 1,3-glycerol carbonate in gas chromatography. In fact, **1** and **2** are known for dimethyl carbonate formation [21–23]. However, we did not find dimethyl carbonate in present reaction condition.

The reaction was sensitive to temperature, pressure and it was observed that the reaction did not occur at ambient temperature and 1 atm CO_2 pressure. Higher temperature prefers for the higher yield till 120 °C and yield drops significantly beyond this temperature, probably due to formation of higher carbonated products. Oligomerization of glycerol carbonate causes the generation of impurities at higher temperature [12]. Effect of pressure was also observed greatly. Although **1** is able to deliver product at milder pressure but we did observe improved yield at higher pressure as well. Thus presumably supercritical condition for CO_2 is preferable for the reaction. Methanol was found to have substantial role in reaction because reaction did not proceed without methanol in present condition. About 25–30 mol% methanol (with respect to glycerol) was required to obtain achievable amount of product.

There was significant difference in the yield seen at below and above boiling point of water (Table 1, entry 3 and 4). Also, increase in yield was observed from 30% to 35% while 13X (soda) zeolite was introduced at 120 °C temperature and 14 MPa CO_2 pressure (Table 1, entry 6 and 7). Such enhancement attributed to absorption of water from the reaction by 13X signifying the requirement of water removal from reaction mixture. The blank run with 13X zeolite (without any catalyst) did not yield glycerol carbonate showing the importance of the catalyst presence. Progress of reaction in time as monitored by GC shows almost no change in yield near 4 h and beyond. This indicates occurrence of equilibrium, which may be the reason for low yield. Such kind of thermodynamic limitations is also known for carbonylations of alcohols [16–24]. Other recyclable dehydrating agents such as 2,2-dimethoxypropane and 1,4-dioxaspiro [4,5] decane [25] also showed comparable result as that of 13X zeolite.

We tried to describe more critically the effect of catalyst concentration, methanol concentration and time as shown in Fig. 1. The plot of time vs. yield in Fig. 1 as described above shows saturation in yield at 4 h and beyond. Moreover, it is having two slopes, which indicates that the reaction may involve two steps. Similarly plots of yield vs. catalyst and methanol concentrations also resemble the dependency of catalyst and methanol in two steps. To check the versatility of **1** we have tried to produce corresponding cyclic carbonate from ethylene glycol and 1,2-propanediol under identical conditions. We found yields of corresponding carbonates at similar condition in 4 h are 35% for glycerol, 42% for 1,2-propane diol and 61% for ethylene glycol. Thus rates of these reactions are in order of ethylene glycol > 1,2-propanol > glycerol. However, it is of our further interest of detailed kinetic study to reinvestigate the effect of diols.

3.2. *Role of methanol*

The reaction with catalysts **1** and **2** in neat conditions at 80 °C and 3.5 MPa CO_2 pressure did not yield any product. Increasing the temperature and pressure did not show any significant difference in the reaction progress. This supports poor activities of **1** and **2** observed in neat reaction conditions by Aresta at higher temperature and pressure (TON 1.14) [8]. Solubility of glycerol in liquid and

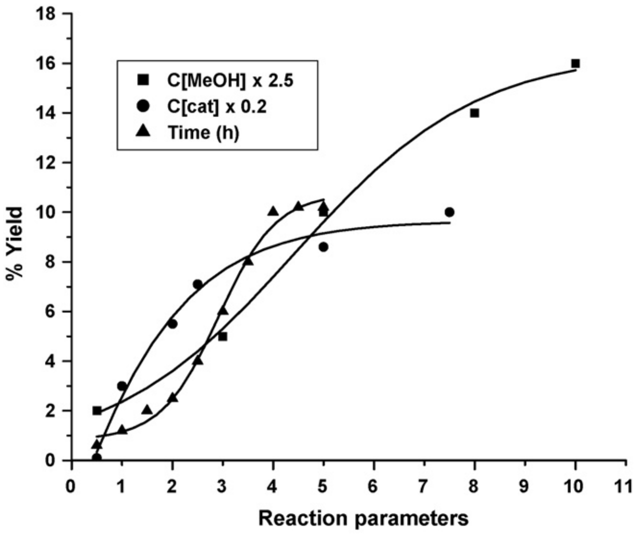
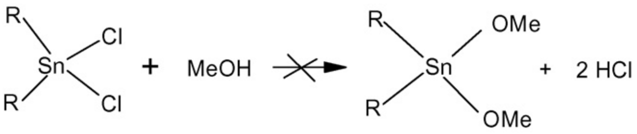


Fig. 1. Variation of yield with catalyst concentration (●, C [cat], mol%) (0.2 g glycerol, 10 mL methanol, 4 h, 80 °C, 3.5 MPa CO_2), methanol concentration (■, C [MeOH], mol%) (0.2 g glycerol, 0.05 g **1**, 4 h, 80 °C, 3.5 MPa CO_2) and time (▲, h) (0.2 g glycerol, 10 mL methanol, 80 °C, 3.5 MPa CO_2). Mol% measured with respect to glycerol, 0.2 g. CO_2 pressure 3.5 MPa and 80 °C temp. used.

$scCO_2$ are 0.3% and 0.5%, respectively, which is too low to take part into reaction [26]. Addition of methanol possibly makes the mixture homogeneous for carrying out the reaction efficiently. Additionally, methanol may be acting as gas expanded liquid (GXL) [27] in reaction condition, is offering a better solvent for dissolution of glycerol and catalyst that effectively accelerates rate and thereby improves the yield.

The reaction with dimethyldigol an inert aprotic polar solvent in place of methanol did not yield any product (Table 1 entry 13). Use of other alcohols, viz., ethanol, propanol and butanol in place of methanol slowed down the rate indicating the solubility may not be the only role of methanol. Interestingly, **2** can form product even in absence of methanol with similar activity as that of **1** in methanol. We found 7.7% yield using 1 mol% **2** at 80 °C and 3.5 MPa in 10 mL dimethyldigol as solvent. However, 25 mol% of methanol (with respect to glycerol) in dimethyldigol solvent was required for **1** to match the activity of **2** under identical conditions suggesting the transformation of catalyst **1** into more active catalyst **2** in presence of methanol [28]. The reaction with di(*n*-butyl)tin(IV)dichloride (**3**) as a catalyst did not yield any product (Table 1 entry 16) demonstrates the inability to generate **2** to replace chloride from **3** by methanol (Eq. (1)) [29], supports our claim of transformation from **1** to **2**.



(1)

We could further support above transformations by ^{13}C NMR and infra red study. While $n\text{-}Bu_2SnO$ was dissolved in methanol ^{13}C NMR shows peak at δ 49.1 ppm (due to $-OCH_3$ group of MeOH) along with a peak at 58.2 ppm (due to $Sn{-}OCH_3$ of. **2**). The solution also shows absence of infra red peak at 1400 cm^{-1} corresponding to $\nu(Sn{=}O)$ (see Section 3.5).

Thus, it is very clear that other than enhancement in solubility of these components, methanol is involved chemically also and thus alter the kinetics of reaction (Fig. 1). However, double slope in Fig. 1 indicates there may be still another step where methanol is involved chemically.

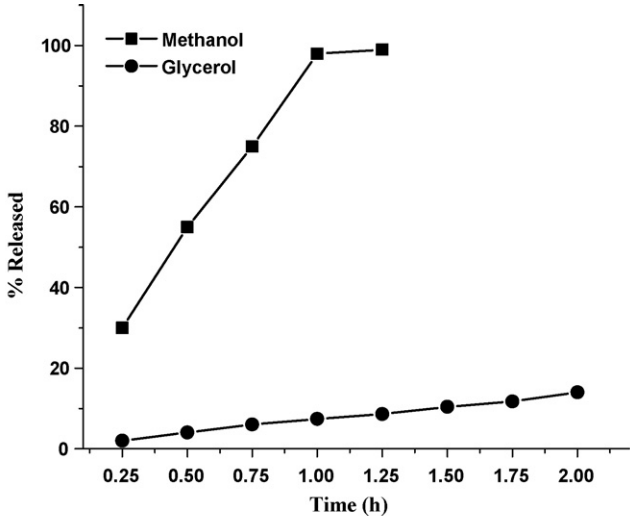


Fig. 2. Competitive alcoholysis of **2** and **4**. Plot of % methanol released from reaction of **2** with glycerol and glycerol released from reaction of **4** with methanol with respect to 100% conversion.

3.3. Formation of di(n-butyl)tinglycerate

The solid obtained upon evaporation of complete homogeneous reaction mixture towards the end of the reaction followed by recrystallization in hexane was completely different from starting **1** in terms of melting point and solubility. Elemental and mass spectral analyses of this solid material was in accordance with tin glycerol complex with a composition of $^{n}Bu_2Sn(OCH_2CHO)CH_2OH$, di(*n*-butyl)tinglycerate (**4**). We have independently prepared **4** by refluxing catalyst **1** and glycerol (1:1, mol) in methanol for 3 h and found a comparable mass, IR spectra and elemental studies as that of literature reported **4** prepared from **2** in toluene [8].

Upon carboxylation of **4** at 80 °C and 3.5 MPa stiochiometric formation of glycerol carbonate (Table 1, entry 17) was observed. Catalyst **4** was able to generate glycerol carbonate catalytically upon addition of methanol and glycerol. Thus, presumably **1** forms glycerol complex **4** in presence of methanol via intermediate **2**.

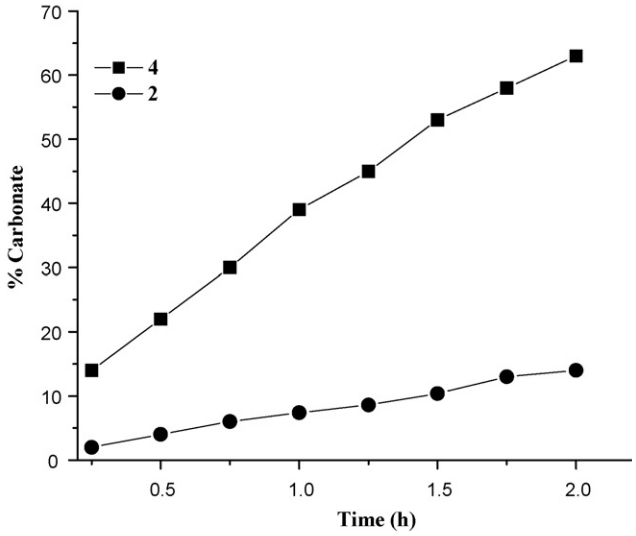


Fig. 3. Competitive carbonation of **2** and **4**. Plot of % dimethyl carbonate produced by carbonation of **2** and glycerol carbonate produced by carbonation of **4** with respect to 100% conversion.

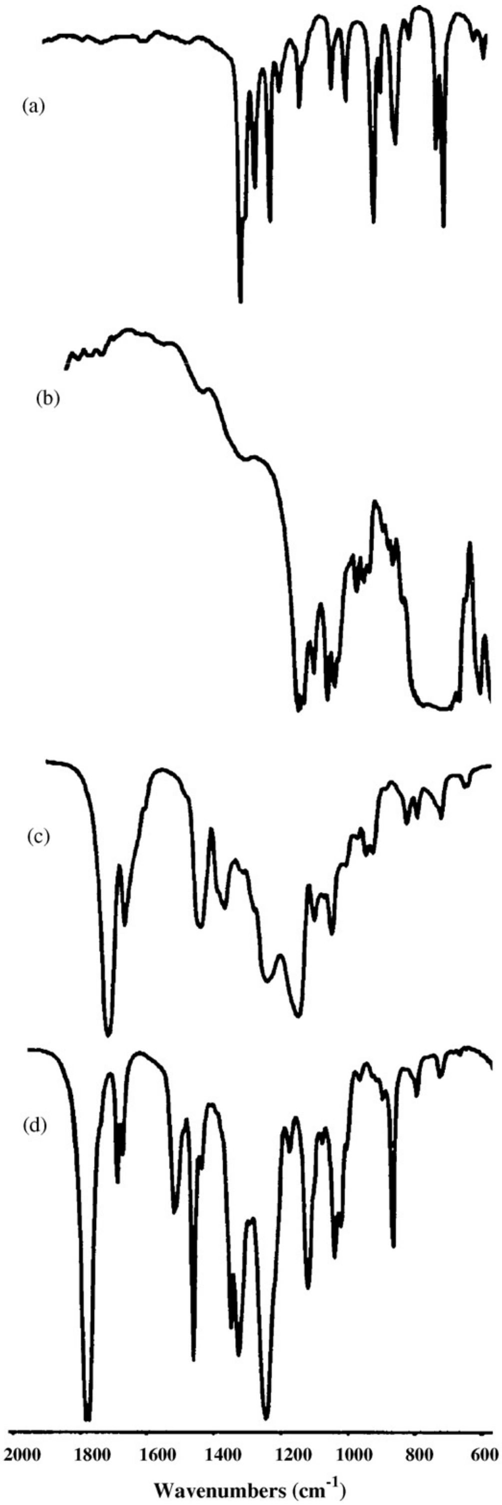


Fig. 4. Infra red spectra (a) of **1** in KBr, (b) of **2** in liquid cell, (c) of **4** in KBr and (d) of reaction mixture in liquid cell.

3.4. *Competitive alcoholysis and carbonation of **2** and **4***

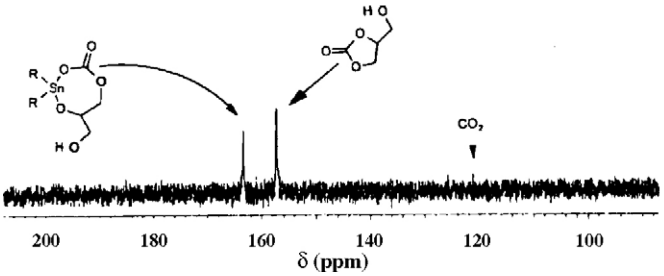


Fig. 5. ^{13}C NMR spectrum of reaction mixture obtained in deuterated methanol (d^4) under CO$_2$ atmosphere.

Absence of dimethyl carbonate as one of the by-products made us curious to study competitive alcoholysis of **1** with methanol and glycerol. Independent reactions **2** with glycerol (Eq. (2)) and **4** with methanol (Eq. (3)) were carried. Respective amount of methanol and glycerol released were measured and plotted in Fig. 2.

$$\mathbf{2} + \text{Glycerol} \rightarrow \mathbf{4} + 2\text{Methanol} \tag{2}$$

$$\mathbf{4} + 2\text{Methanol} \rightarrow \mathbf{2} + \text{Glycerol} \tag{3}$$

Glycerol released from reaction of **4** and methanol is agreed with the results reported by Aresta. A little higher yield of glycerol observed due to amount of methanol used in present case is higher. The difference found in the rate of exchange of respective alcohols is about 20 times higher in case of **2** → **4** (Eq. (2)) than in case of **4** → **2** (Eq. (3)). Thus once **2** is formed it takes almost no time to get converted into **4** leaving a hard chance for reverse reaction to happen. Formation of five membered chelate in **4** may be providing extra stability. This is probably the reason, which dictates carbonation of **4** may be the feasible route for glycerol carbonate formation.

Further, independent of **2** and **4** with CO$_2$ in similar conditions shows faster carbonation of **4** that produces glycerol carbonate than **2** that produces dimethyl carbonate in Fig. 3. In addition, surprisingly, carbonation of **2** in presence of glycerol did not produce dimethyl carbonate. This dictates once **4** formed it undergoes faster carbonation process by the time **2** gets carbonated in present reaction condition. Equilibrium for **2** → **4** also shifts forward (upon carbonation of **4**) giving almost no scope for dimethyl carbonate formation from **2**.

3.5. *Spectroscopic study of reaction mixture*

Our attempt to understand the reaction path way by characterizing the reaction mixture spectroscopically (^{13}C NMR, Mass and IR) showed encouraging results. ^{13}C NMR showed two distinctly different peaks in carbonyl region at 157.5 ppm and 163 ppm (Fig. 5). The peak at 157.5 ppm was corresponding to glycerol carbonates [30] and the other peak appeared in the deshielded region of about 163 ppm correspond to a metal carbonato peak [31] which is essentially the key intermediate generated in combination of catalyst–glycerol–CO$_2$.

Moreover, mass spectrum of reaction mixture showed two peaks at $m/z = 346.00$ and 390.00 corresponding to $[\mathbf{4} + \text{Na}]^+$ and $[\mathbf{4} + \text{CO}_2 + \text{Na}]^+$, respectively. The peak corresponding to [glycerol carbonate + Na]$^+$ at $m/z = 140.19$ was retained with solid mass (see Section 2). This clearly reveals that CO$_2$ has been inserted into **4** there by giving a tin-glycerol carbonated species (**5**). Since Sn–OR bond is known to be susceptible to CO$_2$ [32], **4** possibly forms a 7-membered tin-glycerol-carbonato species (**5**) as described previously by other group [8].

Infra red spectrum of the same mixture (Fig. 4d) showed prominent signals at 1680 cm^{-1} corresponding to $\nu(\text{CO}_3)$ of **5** [8] and peak at 1788 cm^{-1} corresponding to $\nu(\text{CO}_3)$ of glycerol carbonate [12] validating the formation of **5**. However, on prolonged standing, complex **5** slowly turned into olegomeric product, which did not dissolve in most of organic solvents. Absence of peak at 1400 cm^{-1} corresponding to $\nu(\text{Sn{=}O})$ (Fig. 4a) and appearance of peak at 780

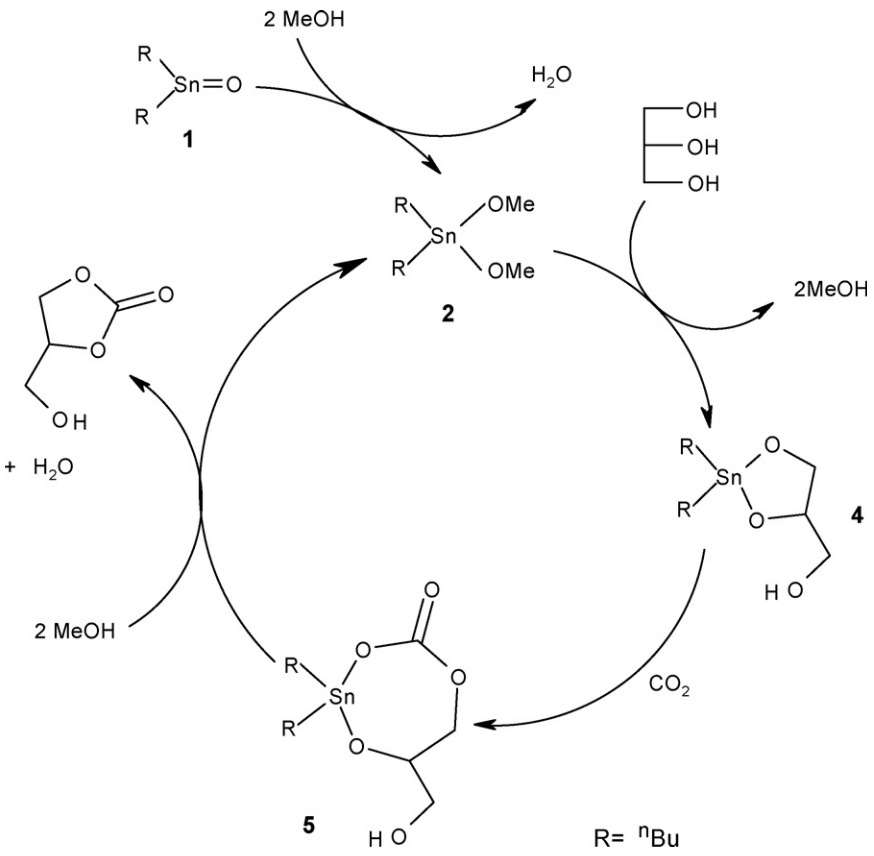


Fig. 6. Plausible reaction path for glycerol carbonate formation.

((Fig. 4b) corresponding to Sn–OMe (matches with authentic sample) during treatment of **1** and methanol confirm the conversion of catalyst **1** to **2** as described above. The broad peak near 3400 cm^{-1} (Fig. 4d) resembles peak corresponding to OH (from glycerol unit) and Sn–OGlycerol, that is different from **2** and **4** (Fig. 4c).

3.6. Mechanism

The above findings together suggest that **1** was activated by methanol to give **2** which in turn react with glycerol forming **4** and undergoes CO_2 insertion leading to glycerol carbonate *via* a tin-glycerolcarbonato complex, **5**. The cycle completes by methanol exchange [33,34] followed by a rearrangement within **5** executing product. The plausible catalytic path way is shown in Fig. 6. These results clearly indicate the methanol dependency in two steps. Two slopes in rate plots (Fig. 1) can also be explained by involvement of two steps namely **1** → **2** and **5** → **2**.

Similar type of mechanism was reported for propylene carbonate formation from propylene glycol and carbon dioxide using **1** in methanol [16]. **1** and **2** showed comparable activities in methanol in case of propylene carbonate formation from propylene glycol and carbon dioxide. The spectral studies confirmed the hypothesis by identifying the characteristics of intermediates. Low or non-catalytic formation of product in case of neat reaction [3] or in presence of water may be due to lack of unavailability of methanol that can bring **5** into catalytic cycle, as **5** is reversible in nature [35,36]. Increase in yield upon addition of methanol probably stops formation of oligomeric species and bring into catalytic cycle as water formed during reaction is removed from system [16]. As mentioned earlier, we have not find dimethyl carbonate therefore, formation of dimethyl carbonate by carbonation of **2** followed by *trans*-esterification with glycerol is ruled out. Because rate of carbonation of **2** is much slower than **4** [8] as can be seen from the GC analyses.

4. Conclusion

Direct carbonation of glycerol (or 1,2 diol) using CO_2 by dibutyltin(IV)oxide ($^{n}Bu_2SnO$), **1** could bring about corresponding cyclic carbonate catalytically in presence of methanol. However, the process requires continuous removal of water to get rid of thermodynamic limitations to higher yield. The reaction proceeds through a tin–glycerol complex which undergoes CO_2 insertion forming a 7-membered key intermediate tin–glycerolcarbonate complex. The key intermediate has a tendency to from oligomer in absence of methanol. Our attempts to develop more robust catalysts for conversion of glycerol to glycerol carbonate are still in process.

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