A study on the carboxylation of glycerol to glycerol carbonate with carbon dioxide: The role of the catalyst, solvent and reaction conditions

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Abstract

Glycerol was reacted with CO_2 (5 MPa) at 450 K in presence of Sn-catalysts (n-Bu$_2$Sn(OMe)$_2$ **1**, n-Bu$_2$SnO **2** or Sn(OMe)$_2$ **3**), using either glycerol or tetraethylene glycol dimethyl ether (tedmg) as reaction medium. **1** was much more active than **2**. **1** was demonstrated to convert into n-Bu$_2$Sn(glycerol-2H) **4** upon reaction with glycerol and elimination of MeOH. Monomeric **4** is proposed to be the active species in catalysis. It converted into a polymeric material with time with consequent reduction of its catalytic activity. Also, after the first catalytic cycle **4** was converted into an oligomeric material that did not contain glycerol. This also caused the reduction of the catalytic activity. **3** was able to uptake CO_2 but was not able to promote the carboxylation of glycerol.

1 and **2** also promoted the *trans*-esterification of dimethylcarbonate (DMC) with glycerol to afford glycerol carbonate, but at a lower rate than the direct carboxylation of glycerol. This fact seems to rule out that the carboxylation of glycerol may proceed through the preliminary formation of DMC and its subsequent *trans*-esterification.
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1. Introduction

The utilisation of glycerol for the synthesis of added value chemicals is a theme of great industrial interest because glycerol is formed in large amounts during the production of biodiesel from natural triglycerids [1], and represents a waste that must be used or eliminated. Several conversion processes [2–7] are described in the literature that transform glycerol into useful materials (see Scheme 1). Among them the synthesis of glycerol carbonate plays a prominent role as the monomer could be used for the synthesis of new functionalised polymers that might have interesting new applications [8].

So far, the only method for the synthesis of glycerol carbonate described in the literature was the *trans*-esterification of ethylene carbonate (EC) or propene carbonate (PC). Either homogeneous or heterogeneous catalysts [9] were used, with a mass ratio of 1:1 with respect to glycerol. Such technology is not completely appropriate also because EC and PC are prepared by carboxyla-

tion of ethene oxide or propene oxide [10] formed, on turn, by epoxidation of the relevant olefin (Eqs. (2a) and (2b) and (3a) and (3b)):

$$C_2H_4 + 1/2 O_2 \longrightarrow \triangle O \tag{2a}$$

$$\triangle O + CO_2 \longrightarrow \text{(ethylene carbonate)} \tag{2b}$$

$$CH_3CH=CH_2 + 1/2 O_2 \longrightarrow \triangle O \tag{3a}$$

$$\triangle O + CO_2 \longrightarrow \text{(propene carbonate)} \tag{3b}$$
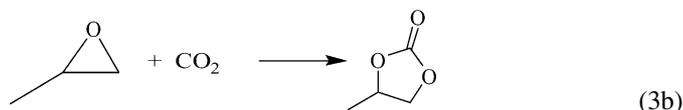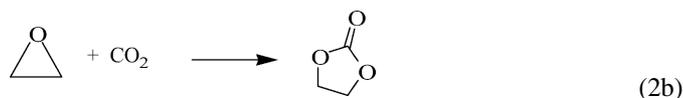
The formation of the epoxide Eqs. (2a)–(3a) is the limiting step in the overall process from the point of view of yield and selectivity, while both the carboxylation of the alkene Eq. (2b)–(3b) and the *trans*-esterification of the alkene carbonate (Eq. (4)) are run with

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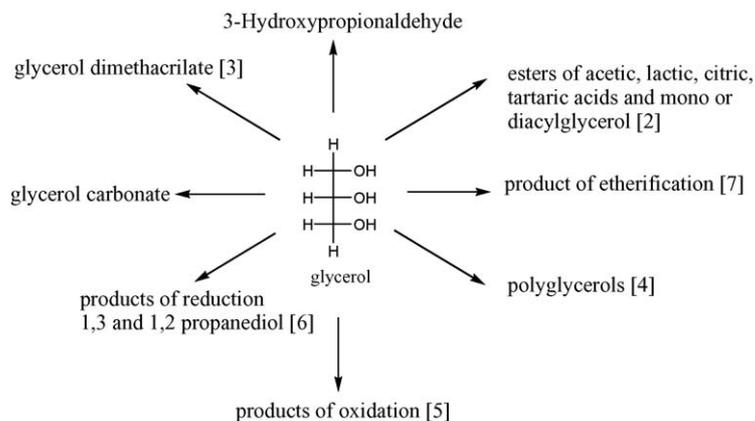
Scheme 1. Processes of conversion of glycerol into useful chemicals.

good yield and selectivity:

(4)
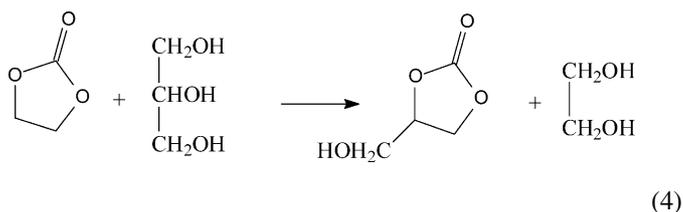
Therefore, finding a new direct route to glycerol carbonate would be very welcome, as it would avoid multi-step processes with energy saving and waste reduction.

The direct carboxylation of glycerol (Eq. (5)) is a very interesting process that would convert

(5)
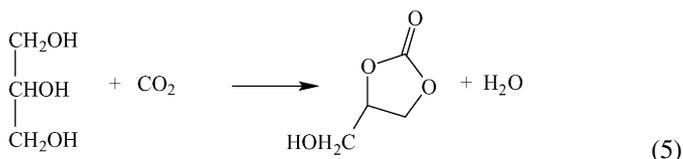
two wastes into a valuable product.

This process has been reported in the literature as "not-occurring" in presence of catalysts such as zeolithes [9]. Following our previous experience in the direct carboxylation of alcohols [11–13] we have investigated the direct carboxylation of glycerol using transition metal alkoxides. In this paper we report the results of our studies on the carboxylation of glycerol in presence of tin-catalysts. The formation of glycerol carbonate takes place, also if with some limitations at the moment.

2. Experimental

2.1. General

All reactions were carried out under dry dinitrogen using the vacuum-line technique. Chemicals (RP grade) were purchased from Aldrich. n-Bu$_2$SnO was used as received. Solvents were further purified [14], distilled and stored under dinitrogen over anhydrous calcium sulphate. CO$_2$ (99.999%) was purchased from Rivoira. High-pressure reactions were conducted in a 100 mL stainless steel autoclave thermostated with an elec-

tric heating jacket (maximum temperature 675 K). The autoclave was equipped with an inner glass jacket to avoid metal contamination of the reagents. Molecular sieves were placed into the glass reactor out of the contact with the liquid phase and used to remove water from the gas phase. Infrared spectra were obtained with a Shimadzu IR Prestige 21 spectrometer, the sample being placed between KBr windows either neat or dispersed in Nujol. Reaction products were analyzed by GC using a capillary column ZB-Wax (30 m × 0.25 mm) on a Agilent 6850 series gas-chromatograph equipped with a flame ionization detector (FID), using diphenyl ether as internal standard. GC–MS analyses were performed using a Shimadzu GC–MS-QP5050. Elemental analysis on tin was conducted colorimetrically [15] using a Shimadzu UV-1601 spectrophotometer.

2.2. Experimental section

n-Bu$_2$Sn(OCH$_3$)$_2$ **1** and n-Bu$_2$SnO **2** were prepared as described in the literature [16].

2.2.1. Synthesis of Sn(OCH$_3$)$_2$

A solution of Na(OCH$_3$) prepared reacting 0.45 g of sodium (19 mmol) in 10 mL of methanol was placed in a three-necked round-bottom flask equipped with a dropping funnel, a condenser and a magnetic stirrer. A solution of SnCl$_2$ (2 g, 10 mmol) in methanol (10 mL) was added dropwise, the mixture was stirred for 1 h at 373 K, then cooled to 300 K and filtered. The solution was concentrated in vacuo to half of its volume and the white solid formed (NaCl) was discarded. Addition of toluene and cooling favoured the formation of a solid that was filtered and analyzed (1.4 g; 74% yield with respect to Sn). The compound contained traces of SnCl$_2$ difficult to eliminate. Anal. Calcd. for C$_{10}$H$_{24}$O$_2$Sn (%): C, 40.82; H, 8.16; Sn, 40.14. Found (%): C, 39.71; H, 7.74; Sn, 41.02. IR (KBr disks, Nujol): bands at 2953 (s), 2910 (s), 2852 (s), 1456 (m), 1375 (m), 1039 (s, ν(C–O)), 568 (w, ν_a(Sn–C$_2$), 484 (w), 451 (m, ν_s(Sn–O$_2$)) cm^{-1}.

2.2.2. Carbonation reaction of Sn(OCH$_3$)$_2$

A 30 mg of solid Sn(OCH$_3$)$_2$ were exposed to CO$_2$ during 10 min in a round bottom flask, avoiding the contact with air, at room temperature. The resulting product was washed with

THF and dried in vacuo. IR (KBr disks, Nujol): bands at 2953 (s), 2910 (s), 2852 (s), 1633 (s), 1456 (m), 1373 (m), 1192 (w), 1097 (m), 1030 (m), 922 (w), 823 (m), 597 (m), 568 (w), 451 (w) cm^{-1}. $Sn(OCH_3)(OCOOCH_3)$ was stable at room temperature in vacuo, in fact the intensity of the CO band at 1633 cm^{-1} did not decrease after pumping in vacuo for 5 h at 373 K. The CO_2 uptake by solid $Sn(OCH_3)_2$ was also followed using a gas burette and shown to stop when the CO_2/Sn molar ratio equal to one was reached.

2.2.3. Synthesis of di(n-butyl)tin glycerate

To a solution of di(n-butyl)tin dimethoxide (0.5 g, 1.69 mmol) in toluene (5 mL), 0.15 g of glycerol (1.69 mmol) were added. The solution was stirred for 24 h at room temperature. The exchange between glycerol and methanol was monitored by gas-chromatography measuring the methanol released (75% after 1 h, 95% in 6 h, 98% in 12 h). The resulting mixture was filtered and the white solid formed was washed with THF (5 mL, two times) and analyzed. Anal. Calcd. for $C_{11}H_{24}O_3Sn$ (%): C, 40.90; H, 7.49; Sn, 36.75. Found (%): C, 41.3; H, 7.40; Sn, 36.2. IR (KBr disks, Nujol): 3272 (s), 2953 (s), 2910 (s), 2852 (s), 1118 (m), 643 (m) cm^{-1}.

2.2.4. Carboxylation of glycerol

(a) *Direct reaction of glycerol with CO_2 without catalyst*: a 2.5 g of glycerol (27 mmol) were placed in the autoclave that was charged with 5 MPa of CO_2. After stirring for 15 h at 453 K, the resulting solution was cooled to room temperature and extracted with 5 mL of acetone (three times). The filtered acetone was analyzed by GC: no glycerol carbonate was formed.

(b) *Use of di(n-butyl)tindimethoxide as catalyst*: a 0.78 g of di(n-butyl)tindimethoxide (2.61 mmol) and 4 g of glycerol (43.5 mmol) were charged in the autoclave with 5 MPa of CO_2. This reaction was carried out using various experimental conditions as reported in Table 1 (see Section 3), that summarizes the results. The resulting solution was cooled to room temperature and extracted with 5 mL of acetone (three times). The acetone solutions were combined and the carbonate recovered by acetone evaporation. The trend of formation of the carbonate is shown in Fig. 1.
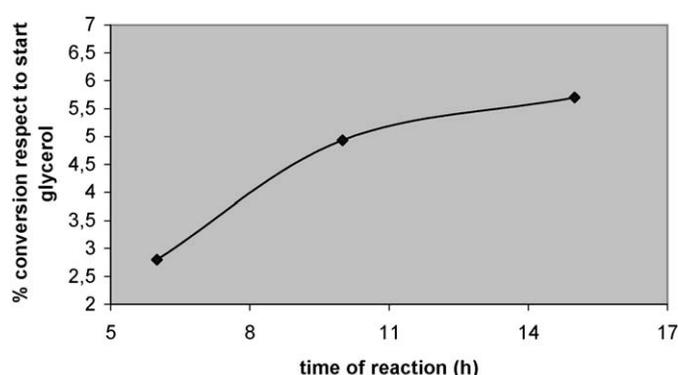

Fig. 1. Trend of conversion of glycerol into glycerol carbonate with n-Bu$_2$Sn(OMe)$_2$ as catalyst. [PCO$_2$ = 5 MPa, 450 K].

(c) *Use of di(n-butyl)tin oxide as catalyst*: the autoclave was charged with 0.65 g of di(n-butyl)tin oxide (2.61 mmol), 4 g of glycerol (43.5 mmol) and 5 MPa of CO_2. After stirring for the given time at 453 K, the resulting product was worked up as in (b). The acetone phase was analyzed by GC. This reaction was carried out under various conditions of CO_2 pressure, temperature and time of reaction. The results are summarized in Table 2 (Section 3).

(d) *Use of tin dimethoxide as catalyst*: a 0.80 g of tin dimethoxide (4.4 mmol) and 4 g of glycerol (43.5 mmol) were charged in the autoclave with 5 MPa of CO_2. Using the same experimental conditions reported for (a)–(c), only traces of glycerol carbonate were revealed.

(e) *Reaction in tetraethylen glycol dimethoxide*: a 0.60 g of di(n-butyl)tindimethoxide (2.04 mmol) and 4 g of glycerol (43.5 mmol) were dissolved in 5 mL of tetraethylen glycol dimethoxide. The resulting solution was placed in the autoclave that was charged with 5 MPa of CO_2. The reaction was carried out for 6 h at 453 K. The results are reported in Table 1.

(f) *Reaction of di(n-butyl)tin(glycerol-2H) with methanol*: to a suspension of di(n-butyl)tin(glycerol-2H) (2 g, 6.21 mmol) in toluene (5 mL), 251 µL of methanol (6.21 mmol) were added, avoiding the contact with air. The solution was stirred for 5 h at 323 K and analyzed by GC. The conversion of the tin-compound into di(n-butyl)tindimethoxide was evaluated by quantitative determination of released glycerol. It

Table 1
Carboxylation of glycerol using di(n-butyl)tindimethoxide as catalyst

Experiment	% Catalyst	Time (h)	PCO$_2$ (MPa)	Temperature (K)	Solvent	Molecular sieves	Glycerol conversion % (isolated)[a]
1	2	15	5	453	None	No	0.42 (0.35)
2	2	15	5	453	None	Yes	2.29 (1.94)
3	2	15	2.5	453	None	Yes	1.74 (1.49)
4	2	15	5	373	None	Yes	0.49 (0.42)
5	2	15	5	453	tedmg[b]	Yes	2.22 (1.88)
6	6	6	5	453	None	Yes	3.30 (2.80)
7	6	10	5	453	None	Yes	5.87 (4.93)
8	6	15	5	453	None	Yes	6.86 (5.72)

In all experiments 4 g of glycerol (43.5 mmol) and 0.78 g of catalyst (2.61 mmol) were used.

[a] The reaction yield was in all cases 15–20% higher than the isolated yield.

[b] tedmg = tetraethylene glycol dimethyl ether.

Table 2
Carboxylation of glycerol using di(n-butyl)tin oxide as catalyst

Experiment	% Catalyst	Time (h)	PCO_2 (MPa)	Temperature (K)	Solvent	Molecular sieves	Glycerol conversion % (isolated)[a]
1	2	6	5	453	None	No	0.36 (0.30)
2	2	6	5	453	None	Yes	1.26 (1.12)
3	2	6	2.5	453	None	Yes	0.94 (0.82)
4	2	6	5	373	None	Yes	0.50 (0.41)
5	2	6	5	453	tedmg[b]	Yes	1.08 (0.97)
6	6	6	5	453	None	Yes	2.30 (1.92)

In all experiments 4 g of glycerol (43.5 mmol) and 0.65 g of catalyst (2.61 mmol) were used.

[a] The reaction yield was in all cases 15–20% higher than the isolated yield.

[b] tedmg = tetraethylene glycol dimethyl ether.

resulted to be: 4% after 30 min, 9% after 1.5 h, 10% after 2.5 h, 10% after 5 h.

2.2.5. trans-Esterification of DMC with glycerol

A 1:1 (molar ratio) mixture of DMC and glycerol (22 mmol for each reagent) was reacted in an autoclave in presence of **1** (22 mmol) under the same conditions of temperature and time as for the carboxylation of glycerol. The reaction products were identified by mass spectroscopy and the methanol exchanged monitored by gas-chromatography. The conversion was shown to be 65% after 15 h.

3. Results and discussion

Glycerol was converted into glycerol carbonate by reaction with CO_2 in presence of n-Bu$_2$Sn(OCH$_3$)$_2$ at 450 K. The reaction was run either in glycerol or in tedmg as solvent (under 5 MPa of CO_2). In the former conditions, glycerol carbonate (crude product) was formed in a 1.14:1 molar ratio (see Table 1) with respect to Sn within 15 h (isolated yield 95% with respect to Sn) and the reaction proceeded, but with a much lower rate, for several hours afterwards. The tin compound isolated at the end of the reaction from the autoclave showed different properties and analyses than the starting catalyst: it resulted to be analogous to the tin-compound recovered from the reaction of carboxylation of methanol in presence of **1**.

Therefore, we decided to investigate the behaviour of n-Bu$_2$Sn(OCH$_3$)$_2$ towards glycerol in absence and presence of CO_2 in order to understand its chemistry.

n-Bu$_2$Sn(OCH$_3$)$_2$ reacted with glycerol at room temperature in toluene with elimination of methanol and formation of n-Bu$_2$Sn(glycerol-2H), **4**. The reaction proceeded with an acceptable rate (see Section 2) and the released methanol was easily monitored by gas-chromatography. A white solid compound slowly separated from the reacting mixture that gave correct analyses for **4** and showed in its IR spectrum a broad band at 3272 cm^{-1} due to ν(OH). This suggests that one OH group of glycerol still bears hydrogen and is not bonded to Sn. A cristallization of the compound was attempted using several conditions that did not afford yet crystals or crystalline-powders suitable for X-ray structure determination. The isolated compound was most probably oligomeric as inferred on the basis of its poor solubility in all organic solvents, except alcohols. However, in the latter solvents an exchange took slowly place and

a mixture of complexes was formed, difficult to characterise. In methanol, for example, the retro-conversion of **4** into **1** was twelve times slower than the reaction of n-Bu$_2$Sn(OCH$_3$)$_2$ with glycerol, but not zero. Studies are still in progress in order to characterise the glycerate-complex in the solid state and in solution. Oligomer **4** did not incorporate CO_2 at room temperature also under 5 MPa, differently from **1** that uptakes CO_2 in toluene under 0.1 MPa of CO_2 [16]. The reaction of **4** with CO_2 took place only at high temperature under 5 MPa of CO_2 but only a small amount of carboxylated complex (νCO at 1681 cm^{-1}) was formed, as demonstrated by an FTIR study under pressure. These data suggest that once monomeric **4** is formed, it can either incorporate CO_2 or oligomerize with deactivation. The fact that glycerol carbonate was formed at a rate comparable with the exchange glycerol–methanol, suggested that the carboxylation of the monomer is faster than the oligomerization. That the monomer is the active species is also demonstrated by the fact that if the oligomer isolated from the exchange of **1** with glycerol was used as catalyst, the catalytic activity was strongly reduced. Once formed, the carboxylated species was able to eliminate glycerol carbonate affording a Sn-compound that resulted to be the same obtained when **1** acted as catalyst in the carboxylation of methanol. It was clearly shown that in the latter reaction, after the first cycle **1** converted into a decamer [17] or trimer [18], depending on the nature of the alkyl group on the alkoxo moiety, with formation of Sn–O–Sn bonds: this conversion slows down the activity of the tin-compounds.

These results demonstrate that if an oligomer is formed, both the reactivity of the complex towards CO_2 and the activity of the catalyst are slowed down. Therefore, one can assume that the mechanism shown in Scheme 2 is operating.

In tedmg, the formation of glycerol carbonate was slower than in glycerol (0.3 mol/mol of catalyst per hour) most probably because of solubility limitation of both glycerol and the complexes.

In order to gather further evidence of the carboxylation of glycerol and exclude that the formation of glycerol carbonate could occur via an alternative route, we have investigated the *trans*-esterification of DMC with glycerol. In fact, one could imagine that **1** might generate DMC and the latter could be then converted into glycerol carbonate by *trans*-esterification. The reaction of DMC with glycerol to afford glycerol carbonate is catalysed by **1**, but the conversion rate is lower than the formation of glycerol carbonate from glycerol and CO_2 in presence of **1**.
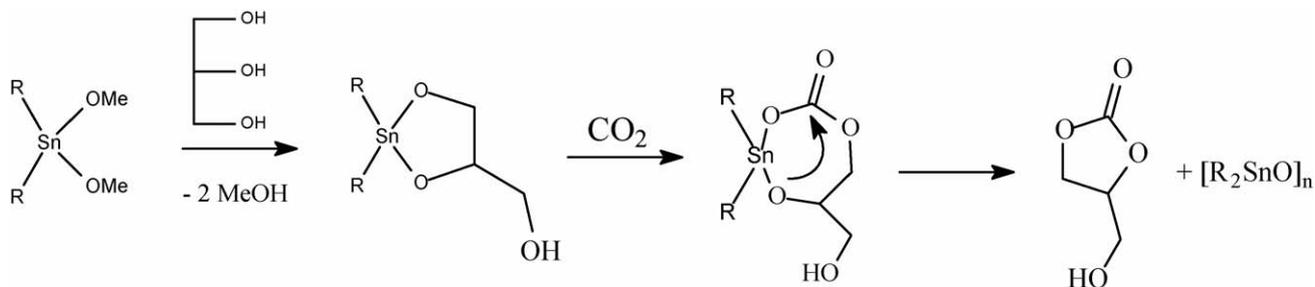
Scheme 2. Reaction mechanism of formation of glycerol carbonate from glycerol and CO_2 under n-Bu$_2$Sn(OMe)$_2$ catalysis.

In fact, while an equimolar solution of **1** and glycerol under CO_2 after 15 h afforded the total conversion of glycerol into glycerol carbonate, the *trans*-esterification of DMC with an equimolar amount of glycerol in presence of **1** gave a 65% conversion after 15 h.

We have also used n-Bu$_2$SnO, **2** and Sn(OMe)$_2$, **3** as catalysts in the direct carboxylation of glycerol.

The latter easily reacted with CO_2 to afford the emicarbonate [(MeO)Sn[OC(O)OMe]]$_n$ **5** that was not able to afford any further reaction. **2** was able to catalyse the formation of glycerol carbonate also if with a low reaction rate (see Table 2).

4. Conclusions

n-Bu$_2$Sn(OMe)$_2$ and n-Bu$_2$SnO were able to promote the direct carboxylation of glycerol into glycerol carbonate. The most active among the catalysts tested was n-Bu$_2$Sn(OCH$_3$)$_2$. The carbonate was formed with an appreciable rate until a 1.14:1 molar ratio of carbonate with the catalyst was reached. Afterwards, the original catalyst was converted into an oligomer which showed a moderate catalytic activity. The monomeric species formed from the reaction of **1** with glycerol was able to react with CO_2 until it was a monomer. The formation of an oligomer reduced the reactivity towards CO_2 and, thus, the catalytic activity.

Acknowledgements

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