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# Investigation of Sn(IV) catalysts in glycerol acetylation



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ABSTRACT

The catalysts dibutyltin dichloride (Bu<sub>2</sub>SnCl<sub>2</sub>), dimethyltin dichloride (Me<sub>2</sub>SnCl<sub>2</sub>), butyltin trichloride (BuSnCl<sub>3</sub>), dibutyltin dilaurate (Bu<sub>2</sub>SnLau<sub>2</sub>), butyl stannoic acid [BuSnO(OH)], and di-n-butyl-oxo-stannane (Bu<sub>2</sub>SnO) were investigated in the acetylation of glycerol (GLY). To the best of our knowledge, this is the first time that this family of catalysts is employed for this reaction and the catalysts bearing chlorine substituents provided the best results. The most active system (BuSnCl<sub>3</sub>) leads to the total conversion of GLY and shows very good selectivity (25.7, 43.5 and 30.8 % for MA, DA and TA, respectively) under mild reaction conditions (80 °C, AA:GLY molar ration of 4:1 with 3 h of reaction). The apparent rate constants ( $k_{ap}$ ) for the GLY conversion confirm these results, since values of 29.1 × 10<sup>-3</sup>, 67.9 × 10<sup>-3</sup> and 87.2 × 10<sup>-3</sup> h<sup>-1</sup> were obtained at 40, 80 and 120 °C, respectively. The activation energy for GLY conversion was determined and for the reaction performed without catalyst the estimated value was 23.9 kJ mol<sup>-1</sup> while using BuSnCl<sub>3</sub> it was 14.3 kJ mol<sup>-1</sup>, representing a decrease of around 50 %.

### 1. Introduction

The development of chemical inputs and fuels from renewable sources has been the subject of intense research and technological development, mainly due to economic and environmental aspects. In this scenario, the production of biodiesel through the transesterification of vegetable oils has increased rapidly in recent years [1–3]. In biodiesel production, glycerol (GLY) forms as the main co-product (10 % by weight) and in order to add value and to make the process more sustainable several reactions are studied [4–13] and GLY esterification is a promising alternative with potential industrial applications [3,14–16].

Acetins or GLY acetals are obtained by reacting GLY with a carboxylic acid, usually acetic anhydride or acetic acid (AA), producing monoacetin (1- and 2-MA), diacetin (1,3- and 1,2-DA) and triacetin (TA) [17,18].

MA is a dense and hygroscopic liquid that is widely applied as a gelatinizing agent, a solvent for paints and in the manufacture of explosives [18]. Similarly, DA is a hygroscopic liquid and is used as a lubricant, softening agent and solvent [19]. In addition, MA and DA are employed in the food and pharmaceutical industries and as building blocks in cryogenics and biodegradable polyester [20]. TA represents 10 % of the global glycerol market and is consumed mainly as fuel additives, such as an anti-knock agent for gasoline, diesel and biodiesel [18]. Its use is also widespread in the production of cigarette filters, as a cellulose plasticizer [19]. Furthermore, it can be applied in the

cosmetics industry, as an emulsifier, perfume fixer and antiseptic [21,22].

The acetylation of GLY is a three-step reaction (Eqs. (1)–(3), and 3 mol of AA is required to react with 1 mol of GLY, in order to accomplish the MA conversion to TA with the release of 3 molecules of water as a by-product [23]. These reactions are reversible and equilibrium-controlled, so several parameters influence the reaction rate, including temperature, molar ratio, type of catalyst and loading (i.e., number of available active sites), and speed of stirring.

$$GLY + AA \rightarrow MA + H_2O \tag{1}$$

$$MA + AA \rightarrow DA + H_2O \tag{2}$$

$$DA + AA \rightarrow TA + H_2O$$
 (3)

This type of reaction is traditionally conducted with catalysts in the homogeneous phase, the most common being sulfuric acid, hydrochloric acid and para-toluenesulfonic acid [18,24]. However, the use of these catalysts is increasingly limited due to environmental problems related to the discharge of effluents with a high degree of toxicity and also due to adverse effects on reaction system due to the high corrosion power [25,26].

In order to overcome these problems, different catalysts have been developed, with notable examples being ion exchange resins [1,23] and heteropolyacids [20]. The esterification of glycerol has been investigated using strong acid ion exchange resins (Amberlyst 15) and

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**Fig. 1.** GLY conversion and MA, DA and TA yields (%) in acetylation of GLY at 40, 80 and 120 °C, as a function of reaction time (min), using a GLY/AA molar ratio of 1:4 in the absence of catalyst and in the presence of BuSnO(OH), Bu<sub>2</sub>SnO and Bu<sub>2</sub>SnLau<sub>2</sub> (ND = not determined; the errors determined were 0.8. 0.5. 0.7 and 0.4 % for GLY, MA, DA and TA, respectively).

acid zeolites (HZSM-5 and HUSY) as catalysts, at 110 °C, with an acetic acid/glycerol molar ratio of 9:1 and reaction time of 4.5 h. It was observed that Amberlyst 15 showed the best results, with a high conversion (above 98 %) and values for selectivity to MA, DA and TA of 33.42, 47.62 and 18.94, respectively [23]. It is important to note that the HZSM-5 and HUSY catalysts can present diffusion problems and their active sites can be deactivated by the formation of water in the reaction [23]. In the studies conducted using p-toluenesulfonic acid (p-TSA), Amberlyst-15 and Amberlyst-36 as catalysts, conversions close to 100 % of glycerol and values for selectivity of 43, 44 and 13 % for MA, DA and TA, respectively, were attained, at 100 °C, with an acid/glycerol molar ratio of 7:1 and 6 h of reaction [27]. The catalytic behavior of mesostructured materials functionalized with sulfonic acid was evaluated and a conversion of up to 90 % of glycerol and more than 80 % selectivity for MA and TA were observed, after 4 h at 125 °C and using an AA/GLY molar ratio of 9:1. According to the authors, the excellent performance obtained is due to the high acid strength of sulfonic acid compared to conventional acid catalysts, such as H<sub>2</sub>SO<sub>4</sub> [25]. The performance of the cesium-supported heteropolyacid catalyst (CsPWA) was evaluated in the glycerol esterification with acetic acid and the results showed that there was a maximum conversion of glycerol (98 %) and selectivity for

MA, DA and TA (25, 58 and 15 %, respectively) at 110 °C, with an AA/GLY molar ratio of 9:1 and 2 h of reaction [20]. Catalysts based on mesoporous carbons were studied in glycerol acetylation and the functionalization of these materials with SO<sub>3</sub>H groups was responsible for the better results obtained at 110 °C, with an AA/GLY molar ratio of 9:1 and 6 h of reaction (conversion of 95 % and values for selectivity for MA, DA and TA of 58, 20 and 22 %, respectively) [28].

There are some examples of the use of Sn(IV)-based catalytic systems in esterification and transesterification reactions, to produce chemicals and biofuels [29–34]. Nevertheless, to the best of our knowledge, no information is available on the performance of this class of catalysts in GLY acetylation to produce MA, DA and TA. In this context, a systematic study employing several Sn(IV) catalysts was carried out and the results are presented and discussed in order to understand the behavior of these systems in this reaction.

# 2. Experimental

#### 2.1. Materials

Dibutyltin dichloride (Bu<sub>2</sub>SnCl<sub>2</sub>), dimethyltin dichloride



Fig. 2. GLY conversion and MA, DA and TA yields (%) in acetylation of GLY at 40, 80 and 120 °C, as a function of reaction time (min), using a GLY/AA molar ratio of 1:4 in the absence of catalyst and in the presence of Me<sub>2</sub>SnCl<sub>2</sub>, Bu<sub>2</sub>SnCl<sub>2</sub> and BuSnCl<sub>3</sub> (the errors determined were 0.8. 0.5. 0.7 and 0.4 % for GLY, MA, DA and TA, respectively).

Table 1

Apparent rate constants ( $k_{ap}$ ) of the GLY conversion relative to the natural logarithm results for the conversion (%) as a function of reaction time (h).

$k_{ap} \ge 10^{-3} (h^{-1})$						
Catalyst	40 °C	80 °C	120 °C			
Without	0.3	2.5	29.2			
Bu <sub>2</sub> SnO	ND	5.5	29.4			
BuSnO(OH)	0.3	7.6	28.4			
Bu <sub>2</sub> SnLau <sub>2</sub>	0.3	5.6	23.7			
Me <sub>2</sub> SnCl <sub>2</sub>	11.9	25.2	68.4			
$Bu_2SnCl_2$	8.7	30.6	68.4			
BuSnCl <sub>3</sub>	29.1	67.9	87.2			

ND = not determined.

(Me<sub>2</sub>SnCl<sub>2</sub>), butyltin trichloride (BuSnCl<sub>3</sub>), dibutyltin dilaurate (Bu<sub>2</sub>SnLau<sub>2</sub>), butyl stannoic acid [BuSnO(OH)], and di-n-butyl-oxostannane (Bu<sub>2</sub>SnO) were purchased from Aldrich. Benzyl benzoate were purchased from Oakwood Chemical, AA and GLY were acquired from Merck (analytical grade). All chemicals were used as received without further purification.

## 2.2. Acetylation of GLY

Acetylation of GLY was performed at room temperature/pressure in a closed batch system, which consisted of 5-mL flasks immersed in an oil bath equipped with a temperature probe and a magnetic stirrer, operating at 3000 rpm. The reactions were carried out using an AA/GLY/CAT molar ratio of x/1/0.166, where x = 3, 4 or 5. Several reaction temperatures were tested (40, 80 or 120 °C) over 15–180 min.

At the end of the reaction, the reaction mixture was placed in an evaporator and left for 5 min to remove unreacted acetic acid. The conversion of GLY (%) and the yields (%) of MA, DA and TA were determined by gas chromatography with flame ionization detector (GC-FID), using a 6 m  $\times$  0.32 mm  $\times$  0.25µm Stabilwax column. The quantification was based on the normalization method with the addition of an internal standard (benzyl benzoate) and the errors were determined as 0.8, 0.5, 0.7 and 0.4 % for GLY, MA, DA and TA, respectively. The samples were analyzed at least in duplicate.

The  $^{13}$ C NMR spectra were acquired at a central frequency of 100 MHz on a Bruker Avance-400 NMR Ultra Shield (9.4 T) spectrometer at 295.15 K, employing a solution of 40 mg of sample in 0.6 ml of deuterated chloroform (CDCl<sub>3</sub>, Aldrich, USA).

# 3. Results and discussion

A series of Sn(IV) complexes was investigated in the esterification of glycerol and acetic acid, in order to investigate the effect of the reaction conditions and the nature of the catalyst on the GLY conversion and selectivity for MA, DA and TA (Figs. 1 and 2). It is important to highlight that this reaction is autocatalytic, since the AA acts as a Bronsted acid catalyst, and the results must be compared to the reaction run without catalyst [34].

Additionally, the values for the GLY conversion, during kinetic control of the reaction, were employed to calculate the apparent rate constants ( $k_{ap}$ ) for the systems evaluated (Table 1). Under isothermal conditions, a pseudo-first-order reaction can be considered, since GLY is considered to be a limiting reactant due to the excess of AA used [35]. Then, treating the data using the natural logarithm of the GLY conversion as a function of reaction time provides straight lines and their



Fig. 3. GLY conversion and MA, DA and TA yields (%) in acetylation of GLY at 80 °C, as a function of reaction time (min), using GLY/AA molar ratios of 1:3, 1:4 and 1:5 without catalyst and in the presence of BuSnCl<sub>3</sub>.

Table 2Chemical shifts (ppm) observed in the  $^{13}$ C NMR spectra of BuSnCl<sub>3</sub> before and<br/>after GLY acetylation and AA contact.

	AA	$BuSnCl_3$	$BuSnCl_3 + AA^a$	$BuSnCl_3 + AA + GLY^a$
C1 carbonyl C2 CH <sub>3</sub> C1 butyl C2 butyl C3 butyl C4 butyl	178.0 20.8 - - -	- - 13.4 25.7 26.8 32.9	177.7 20.8 13.3 25.6 26.9 33.7	176.0 20.8 13.4 25.5 27.0 34.0
MA + DA + TA	-	-	-	170.0-172.0

<sup>a</sup> 80 °C, 1 h, stirring.

slopes give the values for the apparent rate constants ( $k_{ap}$ ), according to Eq. (1).

$$\ln \operatorname{GLY} \% = kt + \ln 100 \tag{1}$$

In general the values of the apparent rate constants  $(k_{ap})$  are consistent in terms of magnitude order with data reported in the literature [20,35,36]. As expected, the temperature has a notable effect in this reaction, even in the absence of a catalyst. In all cases, as the temperature is increased there is a considerable increase in the GLY conversion and this is confirmed by the apparent rate constants  $(k_{ap})$  (Figs. 1 and 2 and Table 1). In addition, the selectivity is strongly influenced by an increase in the temperature, since the formation of TA is

detected mainly at 120 °C in all cases, and at 80 °C for the more active catalytic systems (Figs. 1 and 2). This finding can be attributed to this esterification reaction being endothermic, thus requiring a large amount of heat to drive the process [37]. Therefore, MA formation prevails at 40 and 80 °C, whereas DA and TA are mainly formed at 120 °C.

On analyzing the results, it should be noted that in the reactions conducted with the catalysts BuSnO(OH), Bu<sub>2</sub>SnO and Bu<sub>2</sub>SnLau<sub>2</sub>, at all temperatures, there is no significant difference in comparison with the reactions conducted without a catalyst applying the same temperature and reaction times (Fig. 1), in terms of conversion or selectivity. After 30 min, for instance, in the absence of catalyst no conversion was observed at 40 °C while 23.2 % and 58.4 % of conversion was obtained at 80 and 120 °C, respectively. For these three catalysts the reactivity observed was almost the same, since after 30 min at 80 °C conversions of only 20.3 %, 15.3 % and 15.4 % were observed for BuSnO(OH), Bu<sub>2</sub>SnO and Bu<sub>2</sub>SnLau<sub>2</sub>, respectively. All of these results are corroborated by the apparent rate constants ( $k_{ap}$ ) (Table 1). In terms of selectivity, without a catalyst or using BuSnO(OH), Bu<sub>2</sub>SnO and Bu<sub>2</sub>SnLau<sub>2</sub>, the formation of MA and DA was observed at 80 °C and 120 °C.

In contrast, Me<sub>2</sub>SnCl<sub>2</sub>, Bu<sub>2</sub>SnCl<sub>2</sub> and BuSnCl<sub>3</sub> showed considerable activity even at 40 °C (Fig. 2 and Table 1), where conversions of 24.5, 17.8 and 51.0 %, respectively, were detected after 15 min. The catalysts Me<sub>2</sub>SnCl<sub>2</sub> and Bu<sub>2</sub>SnCl<sub>2</sub> seemed to exhibit comparable reactivity, for instance, the apparent rate constant ( $k_{ap}$ ) at 120 °C was

Table 3

Results taken from the literature related to acetylation of GLY (mentioned in the Introduction) in comparison with the performance of BuSnCl<sub>3</sub>, investigated in this study.

Catalytic system	T (ºC)	AA:GLY	t (h)	GLY conversion (%)	MA/DA/TA (%)	Reference
Mesostructured functionalized materials	125	9:1	4	90	15/45/35	[15]
Amberlyst-15	110	9:1	4.5	80.58	33.42/47.62/18.94	[13]
SAS	105	3:1	3	100	49/51/0	[4]
Wpy-20	110	6:1	10	98	10/25/70	[1]
Sb <sub>2</sub> O <sub>5</sub>	120	6:1	3.5	96.3	33.2/54.2/12.6	[35]
Amberlyst-36	100	7:1	6	100	43/44/13	[17]
Cesium-supported heteropolyacid catalyst (CsPWA)	110	9:1	2	98	25/58/15	[10]
Amberlyst-36	110	8:1	5	95.6	70.3/4.5/0	[18]
BuSnCl <sub>3</sub>	80	4:1	3	100	25.7/43.5/30.8	This study

 $68.4\times10^{-3}\,h^{-1}$  for both. In addition, in the case of the selectivity, no significant differences were observed between these two catalytic systems, with the average formation of around 29.4, 43.2 and 22.0 % of MA, DA and TA.

In the case of  $BuSnCl_3$ , the most active catalyst, high GLY conversions were obtained, with conversions after 15 min of 51.0 % at 40 °C, 78.1 at 80 °C and 92.4 % at 120 °C. After 60 min of reaction, at 80 and 120 °C, the system appeared to have reached equilibrium, exhibiting a conversion of around 95.3 %.

The notable activity of BuSnCl<sub>3</sub> was also illustrated by the apparent rate constants  $(k_{ap})$ , which were  $29.1 \times 10^{-3} h^{-1}$ ,  $67.9 \times 10^{-3} h^{-1}$  and  $87.2 \times 10^{-3} h^{-1}$  at 40, 80 and 120 °C, respectively. Based on these values, the activation energy (AE) related to the GLY conversion in the absence and presence of BuSnCl<sub>3</sub> can be evaluated. Here, the Arrhenius equation derived from transition state theory was considered, in view of the temperature dependence of the reaction rate [36]. In the case of the reaction performed without a catalyst, the estimated AE for the GLY conversion was 23.9 kJ mol<sup>-1</sup> and with the use of BuSnCl<sub>3</sub> it was 14.3 kJ mol<sup>-1</sup>. This reduction of approximately 50 % in the AE on using this catalyst highlights the efficiency of the Sn(IV) catalyst in this process.

The effect of the AA/GLY molar ratio was also investigated, at 80 °C, using BuSnCl<sub>3</sub> and in the absence of catalyst, applying several different reaction times. Fig. 3 reports the results and the values for the apparent rate constant for the GLY conversion.

In the absence of a catalyst, the increase in the amount of AA obtained for the stoichiometric condition (3:1) compared to 4:1 or 5:1 results in a slight increase in the GLY conversion. At a 4:1 M ratio, the observed formation of MA was greater, and this is converted to DA and TA at a 5:1 M ratio. In the presence of BuSnCl<sub>3</sub>, the increase in AA enhances the GLY conversion and almost 100.0 % of conversion is observed at a 5:1 M ratio. However, at a molar ratio of 4:1 a higher amount of TA is observed, while at 5:1 this amount decreased, since it is possible to detected a notable quantity of DA. It is important to highlight that several studies show the dependence, mainly in terms of selectivity, of the ratio of reactants in GLY acetylation [25,35,38–41], and the results presented herein are in line with this finding.

It should be noted that the Sn(IV) catalytic systems investigated in this study present Lewis acidity and empty orbitals that are able to interact with electron donor substrates. In this context, there are two mechanisms established for esterification catalyzed by organotin(IV) complexes, namely, typical Lewis acid coordination or coordination followed by ligand exchange [31]. It is known that organotin(IV) chloride and its carboxylated derivatives act via the typical Lewis acid mechanism, and oxo, alkoxy and hydroxyl derivatives follow the coordination-ligand exchange mechanism [30,31].

Thus, the more active Sn(IV) systems investigated in this study are those that exhibit chloride substituents, even though the oxygen substituents are slightly more electronegative than chlorine, and the mechanism involved is typical Lewis acid coordination. In this case, it can be proposed that the better catalytic performance of these systems is due to less steric hindrance of the substituents present in the systems investigated here, allowing better access of the reactants to the metal center. Additionally, the fact that BuSnCl<sub>3</sub> is more active than Me<sub>2</sub>SnCl<sub>2</sub> and Bu<sub>2</sub>SnCl<sub>2</sub> could be related to the number of alkyl substituents, since as the number of alkyl ligands increases, for organotin(IV) compounds, the Lewis acidity decreases [31]. However, it is important to highlight that it was not possible to observe a difference between the methyl and butyl substituents in terms of their reactivity in the GLY acetylation reactions.

It is should be noted that in a previous study on esterification (using caprylic or acetic acid as model FAs, and methanol-d4) in the presence of Bu<sub>2</sub>SnCl<sub>2</sub> and BuSnCl<sub>3</sub>, <sup>119</sup>Sn NMR investigations and computational studies were conducted and no modifications were observed in the catalysts [33]. Nevertheless, in order to verify if ligand exchange process on BuSnCl<sub>3</sub> takes place during the reaction, GLY acetylation were

performed and analyzed in NMR tubes (see experimental section). If substituent exchange occurs on the catalyst, a displacement of the  $^{13}$ C NMR signals (butyl substituent) and the appearance of new signals related do acetate coordination to metal center are expected. Table 2 summarizes the  $^{13}$ C NMR signals detected after GLY acetylation.

Indeed, these results (Table 2) strongly suggest that there is no modification in the nature of the substituents for  $BuSnCl_3$  during acetylation or in contact with AA. The detection of MA, DA and TA signals in the region of 170.0–172.0 ppm proves that acetylation has occurred [42].

In addition, on comparing the more active system investigated herein with other studies reported in the literature (Table 3), it is possible to observe that the use of BuSnCl<sub>3</sub> leads to the total conversion of GLY and shows promising selectivity (25.7, 43.5 and 30.8 % for MA, DA and TA, respectively) under mild reaction conditions (80 °C, AA:GLY molar ration of 4:1 at 3 h of reaction), showing the good potential of Sn(IV) species to catalyze this type of reaction.

### 4. Conclusions

The catalytic systems based on Sn(IV) species investigated in this study are active in the acetylation of GLY and the most active system, namely BuSnCl<sub>3</sub>, leads to the total conversion of GLY and promising selectivity (25.7, 43.5 and 30.8 % for MA, DA and TA, respectively) under mild reaction conditions (80 °C, AA:GLY molar ration of 4:1 at 3 h of reaction). The apparent rate constants ( $k_{ap}$ ) of the GLY conversion confirms these results and for the reaction performed without catalyst the estimated value of the activation energy for the GLY conversion was 23.9 kJ mol<sup>-1</sup> while the value with the use of BuSnCl<sub>3</sub> was 14.3 kJ mol<sup>-1</sup>, representing a decrease of around 50 %.

## CRediT authorship contribution statement

Débora S. da Silva: Conceptualization, Methodology, Investigation, Writing - original draft. Felyppe M.R.S. Altino: Conceptualization, Methodology, Investigation. Janaína H. Bortoluzzi: Conceptualization, Methodology, Writing - review & editing, Supervision. Simoni M.P. Meneghetti: Conceptualization, Writing review & editing, Supervision, Project administration, Funding acquisition.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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