Catalysis Science & Technology

Accepted Manuscript

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MINIREVIEW

Sn(IV)-based Organometallics as Catalysts for the Production of Fatty Acid Alkyl Esters

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

This paper discusses mechanistic aspects and applications of organotin(IV) catalysts. Particularly, these complexes are employed in a series of industrial reactions in which esters are obtained via (trans)esterification, e.g., polyesters, and lactones. Due to the recent results pointed in the literature, the potential application of this type of catalysts in the synthesis of fatty acid alkyl esters (FAAEs) is also presented.

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MINIREVIEW

Introduction

Although the chemistry of organotin compounds is not often deeply discussed in organometallic textbooks, studies involving tin compounds are quite old! The first organotin compound, diethyltin dichloride, Et_2SnCl_2, was prepared by Frankland in 1849, and this is often considered as the beginning of organometallic chemistry. However, it took almost one hundred years (1943) following the Frankland discovery for the first commercial application of organotin compounds, in which they were used for the stabilization of PVC against heat during processing. From that time, a variety of industrial and biological applications have been subsequently developed.

Organotin compounds are currently the most widely produced organometallic complexes in the world. In terms of catalytic applications, they are employed as catalysts in a series of industrial reactions, in which esters are obtained via (trans)esterification, e.g., in the synthesis of fatty acid alkyl esters (FAAEs),[1] polyesters,[2,3] and lactones.[4]

The catalytic properties of organotin(IV) complexes arise due to their Lewis acid characteristics. Tin atoms are capable of coordinating additional molecules in solution, as well as undergoing associative exchange of certain labile ligands with other compounds in solution (see Figure 1).

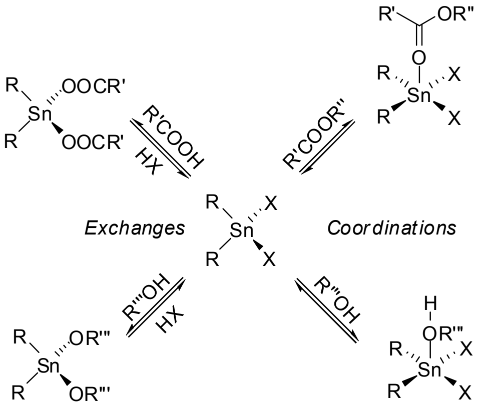


Fig. 1 Coordination of additional ligands and associative ligand exchange.

These characteristics stem from the fact that tin is a metal having empty 5d orbitals, which allows it to expand its coordination number via interaction with non-bonding electron pairs of atoms, most notably oxygen and nitrogen. Even groups bearing non-bonding electron pairs of atoms can act as additional ligands, resulting in intramolecular coordination or intermolecular association to give dimers, oligomers, or polymers (see examples in Figure 2). Thus, all proposed catalytic (trans)esterification mechanisms involving organotin(IV) complexes include ligand association and/or ligand exchange processes.

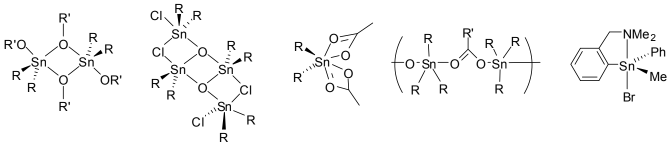


Fig. 2 Chemical structures showing the hypervalent property of organotin(IV) compounds.

Most of the evidence used to elucidate the (trans)esterification reaction mechanism with organotin(IV) complexes is based on exhaustive studies of the catalytic conversion of alcohols and isocyanides for polyurethane production.[5] Polyurethanes are polymers resulting from the reaction between polyols and polyisocyanates in the presence or absence of catalysts (see Figure 3). Here, for the association step, the isocyanate group can be seen as being analogous to the carboxylate group.

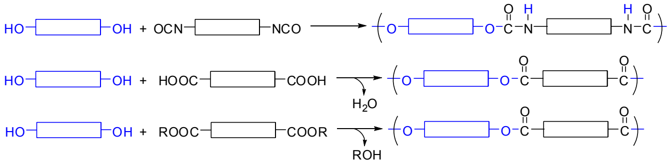


Fig. 3 Polyurethane and polyester formation from alcohols and isocyanides, and alcohols and esters, respectively.

As previously mentioned, the catalytic mechanisms for transesterification and esterification in the presence of organotin complexes are quite similar, but some particularities must be considered for a more rigorous mechanistic proposition. For that reason, we will present our consideration separately below.

It is worth mentioning that Lewis acid catalysts for (trans)esterification reactions are, in general, milder than Brønsted acids and produce a stronger template effect because they are expected to be sterically bulkier than a proton.

Transesterification – Catalytic Mechanism

There are at least two distinct mechanisms that can be proposed for organotin-catalyzed transesterification reactions: Lewis acid mechanisms and exchange/insertion mechanisms, both of which will now be discussed further.[5]

Lewis Acid Mechanism

The Lewis acid mechanism is the most common mechanism proposed for tin-catalyzed transesterification and is shown in Figure 4. There are two possible variations of this mechanism. In both, the tin compound behaves as a classic Lewis acid, first coordinating to the ester through the carbonyl oxygen to polarize the carbonyl.[6] This coordination increases the electrophilicity of the carbonyl carbon toward inter or intramolecular nucleophilic attack by an alcohol, as shown in Figure 4 (A and B, respectively). This mechanism is normally followed by systems in which ligand exchange with the alcohol is not favored.

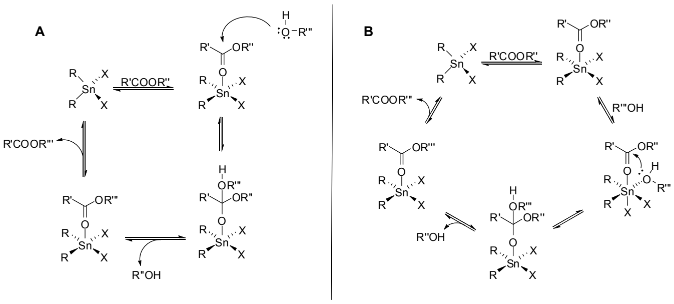


Fig. 4 Illustration of the two organotin(IV)-based catalytic transesterification reactions taking place via the Lewis acid mechanism: A) intermolecular nucleophilic attack and B) intramolecular nucleophilic attack of the alcohol previously coordinated on the metal.

Exchange/Insertion Mechanism

This mechanism involves three basic steps, which are outlined in Figure 5: (1) Associative exchange of the alcohol onto the tin compound; (2) Coordination and insertion of the carboxylic group into the Sn-O bond of the tin alkoxide formed in (1); and (3) Associative exchange of the intermediate.

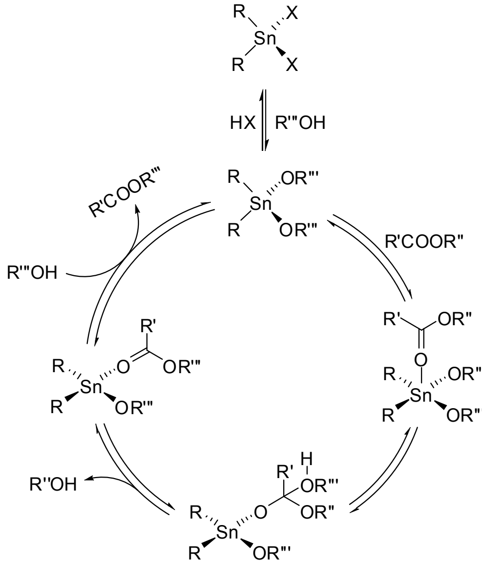


Fig. 5 Illustration of the organotin(IV)-based catalytic transesterification reaction via the exchange/insertion mechanism.

Systematic studies of the use of organotin(IV) complexes as catalysts for transesterification began at the end of the 1960s. In one such study, Pereyre et al. demonstrated that tributyltin alkoxides, R_3SnOR', were able to catalyze transesterification at 120 ºC after 40-100 hours.[7] Later, Poller et al. carried out work on the relative catalytic activity of a series of organotin compounds on the reaction between propyl acetate and methanol,8 and found that the activity decreases in the order $R_2Sn(OAc)_2 > R_2SnO > R_2SnCl_2 > R_2SnS, R_4Sn$. The first two catalysts of this series should pass through a transesterification reaction via the exchange/insertion mechanism, and the latter two follow the Lewis acid mechanism. It is worth mentioning that organotin chlorides are currently considered to not readily undergo alcoholysis, as they appear to carry out the reaction unchanged and to behave as Lewis acids.[2,9]

Other interesting catalytic systems based on organotin(IV) complexes include various tetraorganodistannoxane compounds, $[XR_2SnOSnR_2X]_2$. These compounds possess a stable ladder-like dimeric structure (Figure 6) and are very active in transesterification. The first studies related to the use of these complexes in transesterification reactions were carried out by the group of Otera in the beginning of the 1990s.[10]

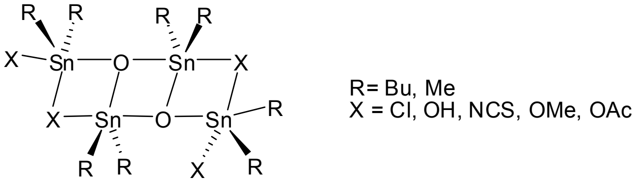


Fig. 6 General structure of tetraorganodistannoxanes.

The proposed mechanism for tetraorganodistannoxane-catalyzed transesterification has been discussed because their application in transesterification reactions. The reaction mechanism for this set of compounds is also based on the two general mechanisms, Lewis acid or exchange/insertion. The primary mechanism followed depends on the nature of the X groups in the structure. Jousseaume and co-workers demonstrated that the tetraorganodistannoxane $[ClBu_2SnOSnBu_2Cl]_2$ is recovered unchanged after the reaction, suggesting that its efficiency in the transesterification comes more from its unique bidentate coordination properties as Lewis acids than from its ability to transfer alkoxide groups.[9]

Esterification – Catalytic Mechanism

As previously mentioned, most organotin(IV)-based catalyzed esterification reactions follow one of two general mechanisms (Lewis acid and exchange/insertion: Figures 4 and 5). However, it should be noted that in esterification reactions catalyzed by organotin(IV), the ligand exchange process is quite important because the protonolysis ability of a carboxylic acid is typically higher than that of an alcohol.

It is additionally worth mentioning that although $SnCl_4$, a popular Lewis acid, is not usually employed in esterification, most other organotin(IV) compounds work quite well (their acidity is tuned by the presence of donating alkyl groups). For example, Me_2SnO is commonly used to catalyze esterification, and the accepted catalytic mechanism is depicted in Figure 7.[11]

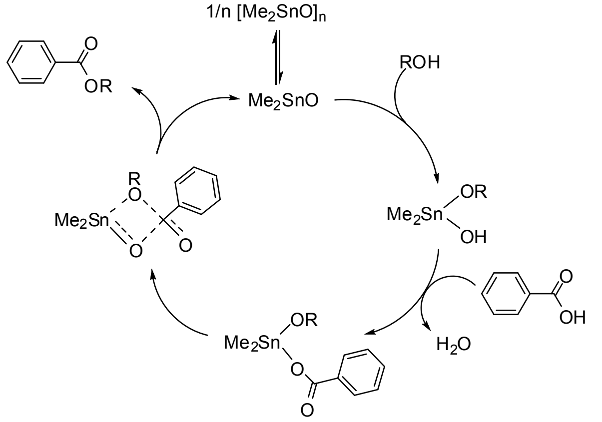
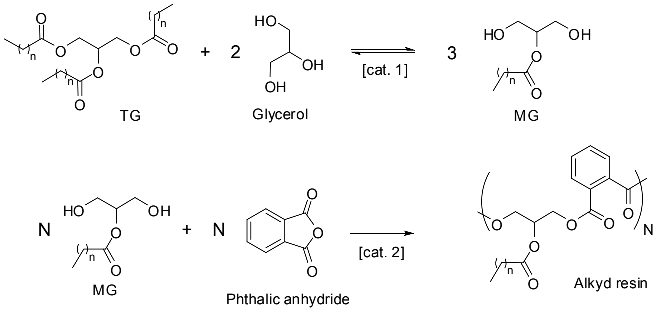


Fig. 7 Illustration of the organotin(IV)-based catalytic esterification reaction using Me2SnO as a catalyst precursor.

Good yields of esters are also obtained when carboxylic acids are treated with catalytic amounts of dichlorotetrabutyldistannoxanes, $[ClBu_2SnOSnBu_2Cl]_2$; however, the dimeric structure is not stable in the presence of the carboxylic acid, and it is quite possible that the monotin compounds formed are responsible for catalyzing the esterification. Furthermore, a release of Brønsted acids such as HCl should also necessarily participate in the catalyzed esterification upon reaction of the dimer with RCOOH.[12]

Industrial application of organotin(IV) compounds as catalysts for (trans)esterification reactions – Synthesis of alkyd resins

The most important industrial use of organotin(IV) complexes as catalysts for (trans)esterification is in the production of alkyd resins. Alkyd resins are polyesters modified by the presence of fatty acids (FAs) or triacylglycerides (TGs) and are largely used in the paint industry. A general example of the synthesis of an alkyd resin is depicted in Figure 8.



where: n= normally 14-16
TG= triacylglyceride
MG= monoacylgliceride
cat. 1= inorganic base
cat. 2= organotin(IV)

Fig. 8 General example of the synthesis of alkyd resins. The TG employed typically contains several unsaturated carbons in the alkyl chain. Figure adapted from Reference 13.

Despite the fact that polyesters themselves generally exhibit very interesting chemical and physical properties, chemical stability, and weathering resistance, it is too difficult to use them directly in paint applications. Therefore, modification of polyesters with FAs or TGs improves some of their properties, primarily durability and flexibility. From a chemical point of view, their main difference from other polyester resins is that alkyd resins contain unsaturated fatty acid side groups.[14]

Alkyd resins can be directly produced from FAs or TGs by acidolysis or alcoholysis.[13,15,16] In the case of synthesis from FAs, which is based on the displacement of fatty acids by polyacids, a polyesterification among the FAs, polyacids, and polyalcohols takes place without the addition of a catalyst.

On the other hand, catalysts can be used in the alcoholysis process (transesterification followed by polyesterification). First, the transesterification of TGs in the presence of polyalcohols generally occurs in the presence of Brønsted bases (e.g., NaOH, KOH, LiOH, CaO, and PbO) between 240 and 270 ºC. If no catalysts are present, temperatures higher than 270 ºC must be employed. For the second step, polyesterification, the use of LiOH, Ca salts, and acidic catalysts such as H_3PO_4, HCl, and H_2SO_4 have been reported. However, in industry large amounts of organotin catalysts are used, some examples of which are displayed in Figure 9.[17]

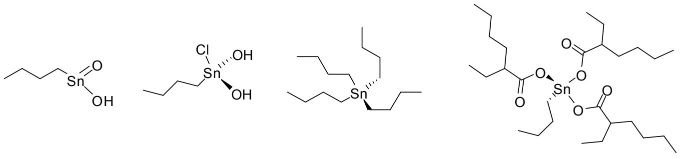


Fig. 9 Chemical structures of some organotin(IV) catalysts employed in the polyesterification reaction of alkyd resins.

For the case of when these reactions are assisted by complexes containing Lewis acid sites, a mechanism in which the active species are generated by a vacant coordination site of metal has been suggested.[6]

Most of the work regarding the synthesis of alkyd resins by alcoholysis involving the use of catalysts has been performed in industrial laboratories, and only a few reports are available in the literature.[5,18] An example of a modified alkyd resin is that produced by alcoholysis of soybean oil with pentaerythritol, followed by esterification with pentaerythritol and phthalic anhydride. Several catalysts (LiOH, dibutyltin oxide (Bu_2SnO), and dibutyltin dichlorid (Bu_2SnCl_2)) are used for alcoholysis and/or esterification reactions. The catalytic system $LiOH/Bu_2SnCl_2$ has proven to be more effective than the conventional method, in which only LiOH is used.[17]

Nevertheless, as already mentioned, the industrial importance of these area leads to development of new materials composed by alkyd resins, and there is some examples of patents that can illustrate these advances. Generally, process modifications are claimed, but the use of well-established tin(IV) catalytic system reinforces the importance of their performance even for new developments.

Bu_2SnO was also employed as catalyst to obtain an alkyd resin for room temperature or thermally curable paints.[19] Dibutyltin dilaurate, $Bu_2Sn(Lau)_2$, was present in the composition of the catalytic system used to obtain a alkyd wood lacquer for home and office decoration, that is considered, environment-friendly, nontoxic and harmless, due the water and alcohol solubility; furthermore, the resin obtained shows suitable properties like: good fullness, good leak tightness, and good hardness.[20] The catalysts Bu_2SnO, and $Bu_2Sn(Lau)_2$ were used in the preparation of acrylic-modified waterborne tall oil alkyd emulsion, used for coating metal and wood and this material exhibits high corrosion resistance and mechanical property.[21]

Another field is the production of aqueous alkyd resin dispersion used for a paint composition such as normal temperature curing paints or thermosetting paints. In this case, several organotin(IV) can be used as butyl stannoic acid (BuSn(O)OH), Bu_2SnO, $Bu_2Sn(Lau)_2$, and SnO_2.[22] Also, $Bu_2Sn(Lau)_2$ is used to obtain aqueous alkyd resin that leads to transparent, and free of turbidity dispersion,[23] as well, to prepare alkyd resin emulsions that are useful as a binding agents for coatings for textiles, mineral materials, metal and wood.[24]

Another interesting application of organotin(IV) species is in the synthesis of alkyd resins in which recyclable raw material is used. In this case, a mixture of Bu_2SnO, and $Zn(OAc)_2$ is used into manufacture of an alkyd resin, using the polyester resin recovered and regenerated from wastes, such as scrap polyethylene terephthalate bottle. This resin presents thermosetting type coating feature, and exhibits a very good transparency.[25]

Potential industrial application – Synthesis of fatty acid alkyl esters for biodiesel and green lubricants

The use of organotin(IV) as a potential catalyst for the production of fatty acid alkyl esters (FAAE) has become a new field of research.[26] Green solvents and lubricants, as well as chemicals and biofuels can be obtained through the esterification and transesterification of FAs and TGs, respectively, catalyzed by organotin(IV) in the presence of short-chain alcohols.[1,27-30] Some of the catalysts that have been previously studied are presented in Figure 10.

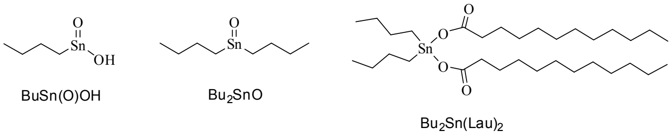


Fig. 10 Molecular structures of butyl stannoic acid, dibutyltin oxide, and dibutyltin dilaurate.

The catalytic mechanisms for esterification and transesterification are based on one of the mechanisms discussed above. It has been suggested that the mechanism includes the formation of a Lewis acid-base complex intermediate through the interaction of the substrate (FA, TG, DG, or MG) with the metal center via the oxygen of the carbonyl group, with subsequent nucleophilic attack by the alcohol (intra or intermolecular) or alkoxide (intramolecular).[1,31]

While $Bu_2Sn(Lau)_2$ is a liquid at room temperature, BuSn(O)OH and Bu_2SnO are insoluble solids in a series of solvents and as previously mentioned are categorized as stable oligomeric structures at room temperature. However, on increasing the temperature these particular arrangements can be destabilized, resulting in more active molecular species.[30,32]

It has been reported that these catalytic systems exhibit better performance at higher reaction temperatures because the catalysts can be more effectively activated and their compatibility in the reaction medium can be improved.[30]

FAAEs via transesterification with organotin(IV) compounds

Transesterification reactions have been investigated using these Sn(IV) complexes ($Bu_2Sn(Lau)_2$, BuSn(O)OH, and Bu_2SnO) while varying several parameters: type of reactors, substrates (source of TG (soybean or castor oils) and various alcohols), temperature, reaction time, and the amount of catalyst (Table 1).[28,30]

The results from reactions conducted using a reactor operating at reflux conditions gave lower yields in comparison with those obtained using a closed steel reactor, in which more severe reaction conditions can be attained (Table 1). This explanation for this behavior can be traced to (i) the amount of methanol present in the liquid phase inside a closed steel reactor (approximately 90-96%), compared with only 35% using a reactor operating at reflux conditions[28] and (ii) the higher degree of solubility and activation of the catalysts that can be reached at the higher temperatures inside the steel reactor.

Table 1 Production of FAMEs (percentage yield) by transesterification in the presence of BuSn(O)OH, Bu_2SnO, and $Bu_2Sn(Lau)_2$ using reflux conditions or a closed steel reactor under different reaction conditions (molar proportions of MeOH:soybean oil:catalyst = 400:100:1; constant magnetic stirring = 1000 rpm).

Reactor	Temperature (ºC)	Time (h)	Catalyst		
			$Bu_2Sn(Lau)_2$	Bu_2SnO	BuSn(O)OH
Reflux conditions	65	1	7	> 5	> 5
		2	11	5.3	> 5
		4	20	6.9	> 5
Close steel reactor	80	1	47	35	-
		2	48	48	10
		4	-	64	-
	120	1	70	45	40
		2	77	83	76
		4	76	83	60
	150	1	98	75	70
		2	98	95	73
		4	80	74	74

Adapted from reference 28

Additionally, five different alcohols (methanol, ethanol, *n*-butanol, *iso*-butanol, and *iso*-propanol) have been investigated to determine the influence of the chemical nature on the reaction yield. Surprisingly, the highest yields were obtained when longer-chained alcohols are employed, mainly at higher temperatures.[28] Considering the mechanism proposed for the transesterification reaction conducted in the presence of catalysts containing Lewis acid sites[31], the expected effects of the chain size or branching in the alcohol chain for this type of reaction are outweighed by the favorable phase equilibrium that is established inside the reactor.

The use of castor oil instead of soybean oil in transesterification was also explored because castor oil is composed almost entirely (ca. 90%) of triacylglycerides containing the unconventional fatty acid known as ricinoleic acid (12-hydroxy-*cis*-octadec-9-enoic acid). The results revealed that regardless of the Sn(IV) catalyst used and reaction conditions employed, the methanolysis of castor oil leads to lower yields than those observed when soybean oil is the source of triacylglycerides. This lower reactivity of the reaction systems based on castor oil cannot be related to mass transfer problems, but rather are due to the singular chemical composition of this oil.[27]

FAAEs via esterification with organotin(IV) compounds

Esterification reactions of soybean FAs with methanol (and in some cases with ethanol) in the presence of these organotin(IV) complexes have been investigated, and the influence of temperature, reaction time, and amount of catalyst was evaluated (Table 2).[1] It is important to mention that esterification can be self-catalyzed due to the presence of Brønsted acid (the fatty acid itself) in the reaction media. For this reason, the catalytic activity of each metal complex must always be compared with the same reaction conducted without the presence of the metal compound.

Table 2 Production of FAAEs (percentage yield) by esterification in the presence of BuSn(O)OH, Bu_2SnO, and $Bu_2Sn(Lau)_2$, and without any catalyst, at several reaction conditions.

Temperature (ºC)	Molar ratio (FFA:ROH:cat)	Time (h)	Alcohol	Catalyst			
				BuSn(O)OH	Bu_2SnO	$Bu_2Sn(Lau)_2$	Without
120	100:400:1	1	MeOH	46	30	22	19
	100:400:1	1	EtOH	27	-	-	20
140	100:400:1	1	MeOH	68	40	35	29
	100:400:1	1	EtOH	58	-	-	29
	100:400:2	1	MeOH	75	44	39	29
	100:400:3	1	MeOH	90	67	40	29
160	100:400:1	1	MeOH	89	60	56	46
		1	EtOH	63	-	-	46
		2	MeOH	91	88	78	67
		3	MeOH	93	91	85	79
		4	MeOH	94	92	90	81

The esterification reactions were run at 120, 140, and 160 ºC using the molar ratio 400:100:1 (alcohol:FA:catalyst), and all of the complexes were found to be active because in their presence better conversions were observed when compared with the self-catalyzed reaction.[1] When the reaction temperature was increased even better results were obtained (Table 2).

The influence of the reaction time on the conversion was evaluated at 160 ºC using durations of 1, 2, 3 and 4 hours. A strong dependence of the conversion on the reaction time during kinetic control of the reaction was observed. BuSn(O)OH was found to be the most active catalyst, with yields of approximately 90% achieved after 1 h. After 3 hours all of the catalysts showed virtually the same tendency, indicating that the system had reached the reaction equilibrium. As expected, in all cases the reaction yields increased when increasing the amount of catalyst, which can be clearly understood because there are more catalytic sites made available.

The use of ethanol leads to lower yields in comparison to those obtained when using methanol at the evaluated conditions. This is because methanol is a stronger nucleophile than ethanol, assisting the nucleophilic attack at the carbonyl group of FA.

In general, during the kinetic control of the esterification reaction, i.e., in the first 2 hours, the order of reactivity observed is BuSn(O)OH >> Bu_2SnO > $Bu_2Sn(Lau)_2$. This order cannot only be related to the different compatibilities of the organotin(IV) species in the reaction medium (see Table 2) because the most soluble one, $Bu_2Sn(Lau)_2$, is not the most active. The observed differences can be related to the different Lewis acidities of the organometallic species, acting directly in the formation of the Lewis acid-base complex intermediate that is formed by the interaction of the substrate (FA, TG, DG, or MG) with the metal center, via the oxygen of the carbonyl group.[31]

It is also encouraging that these catalytic systems are able to simultaneously perform esterification and transesterification reactions of TG and FA. To demonstrate this, three mixtures of FA:TG (50:50, 30:70, and 70:30 wt%) underwent methanolysis in the presence of BuSn(O)OH as the catalyst at 160 °C for 1, 2, 3, or 4 hours (Figure 11).[1]

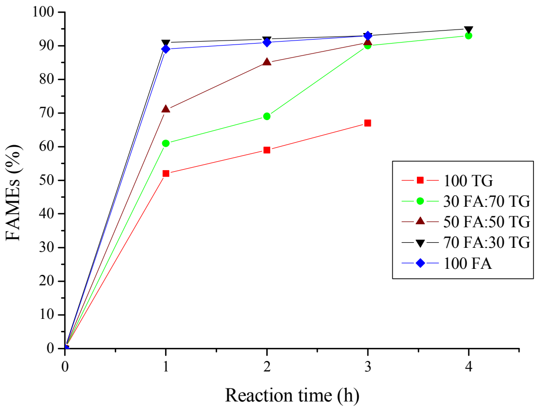


Fig. 11 Yields in terms of FAMEs after methanolysis of soybean FAs, TG, and their mixtures using BuSn(O)OH as the catalyst at 160 ºC.

For the mixture containing 70% FA and 30% TG, conversions of up to 90% after 1 h are achieved. In this case, better yields are obtained because under these experimental conditions the esterification is kinetically favored.

These observations demonstrate that this type of catalyst is quite active for both esterification and transesterification reactions, as well under simultaneous reaction conditions, opening significant possibilities for their use in reactions involving raw materials at low cost and containing a high amount of FAs such as palm oils, recycled oils, and animal fats.[1,12,33]

Final considerations

Mechanistic aspects and industrial applications of organotin(IV) catalysts, which are the most produced organometallic complexes in the world, have been discussed from a critical point of view. A potential industrial application of these catalytic systems, particularly for the synthesis of fatty acid alkyl esters, has been discussed and several promising results were shown, which demonstrate the importance of this research area.

Acknowledgements

Financial support from Brazilian research founding agencies, such as Research and Projects Financing (FINEP), National Counsel of Technological and Scientific Development (CNPq), Federal District Research Support Foundation (FAPDF) and Alagoas Research Support Foundation (FAPEAL), are grateful acknowledged. MRM and SMPM thank CNPq for research fellowships.

This paper is dedicated to Prof. Dr. Roberto Fernando de Souza (*in memoriam*).

Notes and references

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1 Y. C. Brito, D. A. C. Ferreira, D. M. A. Fragoso, P. R. Mendes, C. M. J. de Oliveira, M. R. Meneghetti, S. M. P. Meneghetti, *Appl. Catal. A-Gen*. 2012, **443**, 202.

2 G. Deshayes, F. A. G. Mercier, P. Degee, I. Verbruggen, M. Biesemans, R. Willem, P. Dubois, *Chem-Eur. J.* 2003, **9**, 4346.

3 S. Shyamroy, B. Garnaik, S. Sivaram, *J. Polym. Sci. Pol. Chem.* 2005, **43**, 2164.

4 I. Shiina, *Chem. Rev.* 2007, **107**, 239.

5 A. G. Davies, *J. Chem. Res.* 2010, 181.

6 Y. Roman-Leshkov, M. E. Davis, *Acs Catal.* 2011, **1**, 1566.

7 M. Pereyre, G.Colin, J. P. Delvigne, *B. Soc. Chim. Fr.* 1969, 262.

8 R. C. Poller, S. P. Retout, *J. Organomet. Chem.* 1979, **173**, C7.

9 B. Jousseaume, C. Laporte, M. C. Rascle, T. Toupance, *Chem. Commun.* 2003, 1428.

10 J. Otera, N. Danoh, H. Nozaki, *J. Org. Chem.* 1991, **56**, 5307.

11 G. W. Parshal, S. D. Ittel, Homogeneous Catalysis, 2ª ed., John Wiley&Sons, 1982.

12 E. Crawford, T. Lohr, E. M. Leitao, S. Kwok, J. S. McIndoe, *Dalton Trans.* 2009, 9110.

13 P. A. Z. Suarez, S. M. P. Meneghetti, M. R. Meneghetti, C. R. Wolf, *Quim. Nova* 2007, **30**, 667.

14 Z. W. Wicks, Organic Coatings: Science and Technology, 3rd ed., Wiley-Interscience, Hoboken, New Jersey, USA, 2007.

15 K. H. Wolf, B. Kuster, H. Herlinger, C. J. Tschang, E. Schollmeyer, *Angew. Makromol. Chem.* 1978, **68**, 23.

16 F. S. Guner, Y. Yagci, A. T. Erciyes, *Prog. Polym. Sci.* 2006, **31**, 633.

17 D. Doulia, S. Rokotas, K. Georgopoulou, *Surf. Coat. Int. B: Coat. Trans.* 2006, **89**, 215.

18 L. S. Ratliff, L.J. Prendny, Catalysts for use in the acidolysis, alcoholysis and esterification reactions of polyesters for coating resins, Advances in Coating Technology, ACT'98, International Conference, 3rd, Katowice, Poland, 1998.

19 I. Kei, K. Tsutomu, N. Reijiro, N. Nobushige, Kansai Paint Co Ltd., *JP2002179777-A* **2002**

20 Y. Guo, *CN103013308-A* **2013**

21 J. Yang, W. Kuang, Y. Liu, Y. Jia, C. Liu, *CN102796228-A* **2012**

22 C. Kawamura, K. Ito, K. P. C. Ito, *EP1245603-A1* **2002**

23 C. Kawamura, K. Ito, I. Yoshihara, N. Numa, *WO200125309-A* **2001**

24 E. Urbano, M. Gobec, O. Ferk, *EP1092742-A* **2003**

25 C. Kawamura, K. Ito, *JP2002317035-A* **2002**

26 U. Schuchardt, R. Sercheli, R. M. Vargas, *J. Brazil. Chem. Soc.* 1998, **9**, 199.

27 T. M. Serra, D. R. de Mendonça, J. P. V. da Silva, M. R. Meneghetti, S. M. P. Meneghetti, *Fuel* 2011, **90**, 2203.

28 D. R. de Mendonca, J. P. V. da Silva, R. M. de Almeida, C. R. Wolf, M. R. Meneghetti, S. M. P. Meneghetti, *Appl. Catal. A-Gen.* 2009, **365**, 105.

29 J. Dupont, P. A. Z. Suarez, M. R. Meneghetti, S. M. P. Meneghetti, *Energy Environ. Sci.* 2009, **2**, 1258.

30 D. A. C. Ferreira, M. R. Meneghetti, S. M. P. Meneghetti, C. R. Wolf, *Appl. Catal. A-Gen.* 2007, **317**, 58.

31 B. A. D. Neto, M. B. Alves, A. A. M. Lapis, F. M. Nachtigall, M. N. Eberlin, J. Dupont, P. A. Z. Suarez, *J. Catal.* 2007, 249, 154.

32 C. Elschenbroich, Organometallics, 3rd ed., Wiley-VCH, Weinheim, Germany, 2006.

33 M. B. Alves, F. C. M. Medeiros, P. A. Z. Suarez, *Ind. Eng. Chem. Res.* 2010, **49**, 7176.