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Mono-organotin(IV) compounds as esterification and transesterification catalysts

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A series of monoorganotin(IV) compounds has been investigated as transesterification catalysts for the reaction of butyl propionate with methanol. The most active catalysts were found to be those which contain tin–halogen bonds, e.g. monobutyltin trichloride ($BuSnCl_3$), and the least effective were the coordinatively saturated mono-organotin derivatives. Certain of the mono(2-carboalkoxyethyl)tin compounds were found to undergo a facile autocatalysed transesterification reaction with alcohols. Coordination of the carbonyl group in the ester to the tin catalyst is an important factor influencing its activity. A study of the catalysis of the esterification of propionic acid by $BuSnCl_3$ is reported.

Keywords: Monoorganotin compounds, transesterification catalysts, mono(2-carboalkoxyethyl)tin derivatives.

INTRODUCTION

Tin chemicals, especially di- and mono-alkyltin(IV) and tin(II) compounds, are widely used in industry as homogeneous catalysts, their consumption accounting for at least 1000 tonnes of tin metal per annum at the present time. They are principally utilized as catalysts in the manufacture of polyurethane foams, as cross-linking agents for room-temperature vulcanizing (RTV) of silicone rubbers and as catalysts for esterification/transesterification reactions.[1] Additionally, laboratory studies have demonstrated their effectiveness as catalysts for the formation of polycarbonates,[2,3] for the dehydration of alcohols to ethers[4–6] and in the synthesis of macrolides.[7]

The use of organotin catalysts for esterification and transesterification reactions has become increasingly important in recent years, since these compounds function in a neutral medium and, therefore, any risk of corrosion of the reaction vessel is minimized. Three of the catalysts have recently been approved by the US Food and Drug Administration (FDA) for use in food grade formulations.[8]

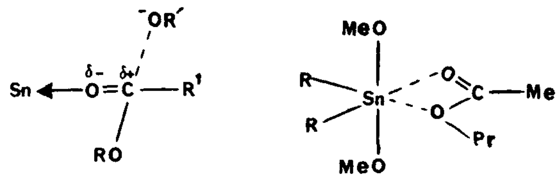

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Figure 1

In earlier studies of these systems, Ross[9] proposed that a simple Lewis acid mechanism was operational, in which coordination of the ester carbonyl group to the tin atom polarizes the carbonyl bond, thereby making the carbonyl carbon more susceptible to attack by a nucleophilic reagent, such as an alcohol (**I**, Fig. 1). Later investigations by Pereyre *et al.*[10] of the catalysis of transesterification by organotin alkoxides envisaged catalysis proceeding via an alkoxy exchange route (Eqns [1] and [2]).

$$R_3SnOR^1 + R^2OH \rightleftharpoons R_3SnOR^2 + R^1OH \qquad [1]$$

$$R_3SnOR^2 + R^3COOR^1 \rightleftharpoons R_3SnOR^1 + R^3COOR^2 \qquad [2]$$

Poller and Retout[11] also postulated organotin alkoxides as the active catalytic species, based upon observations that, in a series of diorganotin compounds tested as catalysts for the transesterification of propyl acetate with methanol, those exhibiting the highest activity were the acetate and oxide derivatives which, it was suggested, would be expected to form alkoxides more readily. They proposed that a hexacoordinate intermediate (**II**, Fig. 1) was formed between the alkoxide and the ester, which functions as a bidentate ligand.

Ester carbonyl coordination to tin(IV) has been demonstrated[12] crystallographically in the six-coordinate complex, $SnCl_4 \cdot 2EtOCOCH{=}CHPh$, in which ethyl cinnamate acts as a monodentate donor group.

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Dibutyltin dicarboxylates were observed[13] by Jones and Nottingham to be highly selective catalysts for the transesterification of alkyl 3-alkoxypropionates (Eqn [3]), and Otera and coworkers found[14] that 1,3-disubstituted tetrabutyldistannoxanes performed well in many systems.

$$R^3OCR_2CR_2COOR^1 + R^2OH \rightarrow R^3OCR_2CR_2COOR^2 + R^1OH \quad [3]$$

In Malaysia, studies have been carried out on a range of inorganic tin(II) and organotin(IV) compounds as esterification catalysts for fatty acids derived from palm oil and it was concluded that the mono-organotin compound $BuSnCl_3$ was the most active.[15]

In the course of preparing anionic (2-carboalkoxyethyl)halogenostannate complexes,[16] we observed, while carrying out recrystallizations from various alcohols, that (2-carboalkoxyethyl)tin trichlorides and some of their complexes underwent a facile autocatalysed transesterification reaction with the refluxing alcoholic solvent (Eqns [4]–[6]). Poller and Retout found[11] that a similar transesterification occurred in the attempted conversion of $(2\text{-}MeOC_6H_4)_2SnX_2$ to $(2\text{-}MeOC_6H_4)_2Sn[SCH_2COO(iOct)]_2$ in methanol, when the methyl thioglycollate ester was recovered.

$$BuOCOCH_2CH_2SnCl_3 + R^1OH \xrightarrow{\Delta} R^1OCOCH_2CH_2SnCl_3 + BuOH \quad [4]$$

$$BuOCOCH_2CH_2SnCl_3 \cdot L_2 + R^1OH \xrightarrow{\Delta} R^1OCOCH_2CH_2SnCl_3 \cdot L_2 + BuOH \quad [5]$$

$$(Me_4N)_2[EtOCOCH_2CH_2SnCl_5] + MeOH \xrightarrow{\Delta} (Me_4N)_2[MeOCOCH_2CH_2SnCl_5] + EtOH \quad [6]$$

$R^1 = Me, Et, Pr, iPr$; $L_2 = 2,2'$-bipy or 1,10-phen.

In this paper, studies have been carried out on the transesterification of methanol with mono(2-carboalkoxyethyl)tin derivatives, on the possible use of these and, in view of the results of Tanaka *et al.*[17] and Arifin *et al.*,[15] of other monoorganotin(IV) compounds as transesterification and esterification catalysts, and on the probable reaction mechanism involved.

EXPERIMENTAL

Synthesis of mono-organotin catalysts

The mono-organotin trichlorides (and dibutyltin oxide) were obtained from Schering AG and Akzo Chemie and the other mono-organotin catalysts were prepared by literature methods (with the exception of the new compounds described below), their microanalyses, melting points and/or boiling points being in good agreement with those reported previously.[16, 18–22] The microanalytical determinations were carried out by Mr A. Stones in the Chemistry Department, University College London.

$(Me_4N)_2[MeOCOCH_2CH_2SnCl_3F_2] \cdot 3H_2O$
$(Me_4N)_2[BuOCOCH_2CH_2SnCl_3F_2] \cdot H_2O$[16] (0.3 g, 0.54 mmol) was refluxed in excess methanol (15 cm^3) for two hours and the solvent was concentrated by evaporation. The product, which was hygroscopic, was filtered and washed with cold methanol. Found (Calcd for $C_{12}H_{37}O_5N_2SnCl_3F_2$): C, 26.66 (26.09); H, 5.76 (5.66); N, 4.79 (5.07); Cl, 21.32 (19.27)%.

Table 1 Activity of mono-organotin catalysts in the transesterification reaction $EtCOOBu + MeOH \rightarrow EtCOOMe + BuOH$

Compound	Percentage conversion after 2 h[a]
$BuSnCl_3$	39
$OctSnCl_3$	28
$BuOCOCH_2CH_2SnCl_3$	44
$BuOCOCH_2CH_2SnCl_3 \cdot$ bipy	20
$(Et_4N)_2[BuSnCl_3Br_2]$	37
$BuSn(OH)_2Cl$	14
$BuOCOCH_2CH_2Sn(SCSNEt_2)_3$	3
$BuSn(OSiPh_3)_3$	0
$BuSn(OCOMe)_3$	0
$[BuSn(O)OCOMe]_n$	0
$(Bu_2SnO)_n$	17
Control	0

[a] Determined by GC analysis, after quenching the reaction in a sodium chloride/ice bath. Conc. of catalyst 0.2 mol% with respect to the ester.

Table 2 Transesterification of (2-carboalkoxyethyl)tin compounds with methanol

Compound	$\nu_{as}(CO)$ (cm^{-1})	Coordination no. of Sn	Product[a]
$BuOCOCH_2CH_2SnCl_3$	1640	5	$MeOCOCH_2CH_2SnCl_3$
$BuOCOCH_2CH_2SnCl_3 \cdot bipy$	1724	6	$MeOCOCH_2CH_2SnCl_3 \cdot bipy$
$BuOCOCH_2CH_2SnCl_3 \cdot phen$	1724	6	$MeOCOCH_2CH_2SnCl_3 \cdot phen$
$(Me_4N)_2[EtOCOCH_2CH_2SnCl_5]$	1724	6	$(Me_4N)_2[MeOCOCH_2CH_2SnCl_5]$
$(Me_4N)_2[BuOCOCH_2CH_2SnCl_3F_2] \cdot H_2O$	1724	6	$(Me_4N)_2[MeOCOCH_2CH_2SnCl_3F_2] \cdot 3H_2O$
$K_2[BuOCOCH_2CH_2SnF_5]$	1724	6	No reaction
$BuOCOCH_2CH_2Sn(SCSNEt_2)_3$	1724	7	Complex decomposed
$(BuOCOCH_2CH_2Sn)_4S_6$	1724	4	Complex decomposed
$BuOCOCH_2CH_2SnBu_3$	1724	4	No reaction

[a] After 2 h reflux in methanol.

$(BuOCOCH_2CH_2Sn)_4S_6$
(2-Carbobutoxyethyl)tin sesquisulphide was prepared by the dropwise addition of a concentrated aqueous solution of sodium sulphide hydrate (4.4 g, 16.9 mmol if taken as 30% w/w Na_2S) to a stirred solution of (2-carbobutoxyethyl)tin trichloride (4.0 g, 13.0 mmol) in acetone. The white solid which formed was filtered off and recrystallized from acetone, to give a small amount (10% yield) of a hard white crystalline product, m.p. 159–176°C. Found (Calcd for $C_{28}H_{52}O_8S_6Sn_4$): C, 27.97 (28.41); H, 4.41 (4.43); S, 15.53 (16.25)%.

$BuOCOCH_2CH_2Sn(SCSNEt_2)_3$
A solution of (2-carbobutoxyethyl)tin trichloride (1.0 g, 2.8 mmol) in chilled methanol was added to a filtered solution of sodium diethyldithiocarbamate trihydrate (3.8 g, 16.9 mmol) in the same

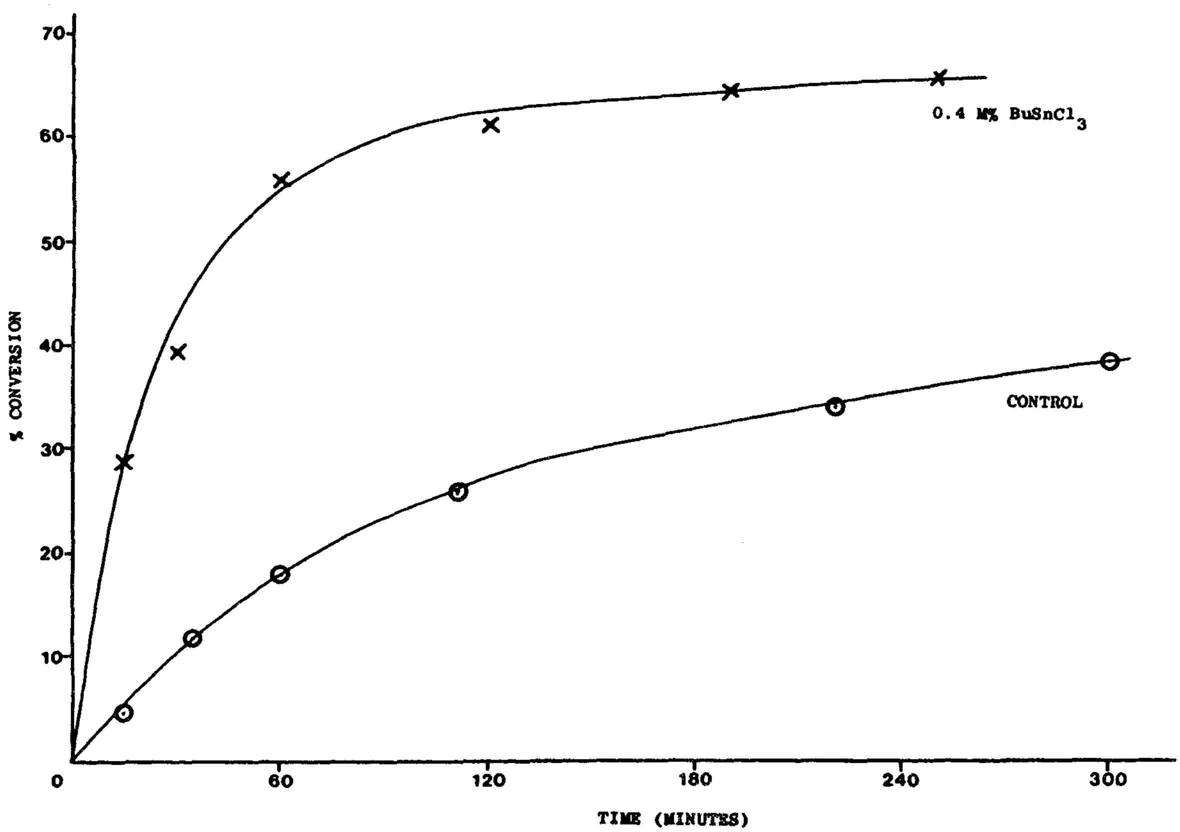

Figure 2 Catalysis of the esterification of propionic acid by $BuSnCl_3$.

Table 3 Catalysis by $BuSnCl_3$ of the reaction $EtCOOH + BuOH \rightarrow EtCOOBu + H_2O$

Catalyst	Time (min)	Mean of two titrations with 1 mol dm^{-3} NaOH[a] (cm^3)	Conversion (%)
Control	0	2.90	0
	15	2.77	4.5
	35	2.56	11.7
	60	2.38	17.9
	110	2.16	25.5
	220	1.92	33.8
	300	1.79	38.7
$BuSnCl_3$[b]	0	3.00	0
	15	2.14	28.7
	30	1.82	39.3
	60	1.33	55.7
	120	1.17	61.0
	180	1.06	64.7
	250	1.02	66.0

[a] See Experimental section. [b] 0.4 mol %.

(cold) solvent. On standing overnight in a cool place, pale yellow needles of the product crystallised in 82% yield, m.p. 85–88.5 °C. Found (Calcd for $C_{22}H_{43}O_2N_3S_6Sn$): C, 38.15 (37.67); H, 6.26 (6.36); N, 6.07 (6.00); S, 27.77 (27.28)%.

Infrared spectra

Infrared spectra were recorded as liquid films, nujol mulls or KBr discs using a Grubb–Parsons Spectromaster Mark 1 instrument.

GC measurements

GC determinations were carried out on a Perkin–Elmer F11 instrument with a flame ionization detector. Column conditions were as follows: 4 m $\frac{1}{8}$-in (3 mm) o.d. column packed with $2\frac{1}{2}$% OV-17 on Chromosorb G AW DMC 80–100 mesh; carrier gas nitrogen at 18 lbf in^{-2} (125 kPa); temperature 74 °C; amplifier range 50×10^2.

Percentage conversions in the transesterification between butyl propionate and methanol were calculated from the ratio of calibrated peak integrals for butanol and butyl propionate.

Esterification study

Equimolar (0.25 mol) quantities of propionic acid and butanol were refluxed together in the presence and absence of 0.4 mol% $BuSnCl_3$ catalyst. At measured intervals, samples of the reaction mixture were withdrawn by syringe through a rubber septum and quenched by discharging into sealed containers in a sodium chloride/ice bath. Two 0.5 cm^3 aliquots of each quenched sample were then titrated with 1 mol dm^{-3} aqueous sodium hydroxide and the mean titration figures were used to calculate the percentage conversion.

RESULTS AND DISCUSSION

The activities of a series of mono-organotin(IV) catalysts (and dibutyltin oxide) are compared in the transesterification reaction between butyl propionate and methanol in Table 1.

In agreement with Arifin *et al.*,[15] those mono-organotin compounds containing tin-halogen bonds were found to be more active, compared with the control, than the oxygenated tin catalysts. This could be due to the ability of the former derivatives to coordinate to the ester carbonyl,[9] thereby activating the ester OR group to nucleophilic attack by $R'O^-$ [see (**I**), Fig. 1]. In accord with this suggestion, the IR spectrum of an equimolar mixture of the $BuSnCl_3$ and ethyl acetate showed a shift of $\nu_{as}(CO)$ from 1725 cm^{-1} in the free ester to 1666 cm^{-1} in the 1:1 mixture. The observed catalytic activity of the halgenostannate complex, $(Et_4N)_2[BuSnCl_3Br_2]$, in which the tin atom is six-coordinate in the solid state, may be rationalized in terms of its coordination to the ester carbonyl to form a heptacoordinate adduct or, alternatively, by its partial dissociation under the conditions prevailing in the reaction to yield free $BuSnCl_3$ (which can coordinate to the ester). The similar percentage conversions obtained for this complex and for $BuSnCl_3$ would favour the latter explanation. Ester carbonyl→tin coordination would explain why, in the transesterification reactions of 3-alkoxypropionates studied by Jones and Nottingham (Eqn [3]),[13] the OR^1 moiety in closest proximity to the carbonyl group is selectively attacked by the R^2O^- nucleophile from the alcohol.

Further evidence for the importance of coordination of the ester carbonyl group to the tin catalyst may be obtained from the (2-carboalkoxyethyl)tin compounds, such as $BuOCOCH_2CH_2SnCl_3$, which can be regarded as resulting from the replacement of a β-hydrogen atom in butyl propionate by a Cl_3Sn moiety—thereby incorporating the organotin catalyst within the ester molecule—and which contains[16] an intramolecularly coordinated ester carbonyl group. As well as being an active catalyst for the methanolysis of butyl propionate (Table 1), this compound is itself completely transesterified after two hours in refluxing methanol to form $MeOCOCH_2CH_2SnCl_3$ (Eqn [4], $R^1 = Me$, and Table 2). In contrast with this, the compound $Bu_3SnCH_2CH_2COOBu$, which is a very weak Lewis acid tetraorganotin showing little tendency to increase its coordination number above four, undergoes no autocatalysed transesterification under the same conditions (Table 2). The bipyridyl complex of (2-carbobutoxyethyl)tin trichloride exhibits a lower catalytic activity than the parent trihalide on the basis of its weaker Lewis acidity and the hepta-coordinate complex, $BuOCOCH_2CH_2Sn(SCSNEt_2)_3$, in which the intramolecular carbonyl oxygen→tin coordination does not occur, in order to accomodate three bidentate dithiocarbamate ligands [cf. $MeOCOCH_2CH_2Sn(SCSNMe_2)_3$][23] shows an even greater reduction in catalytic effect (Table 1).

The heptacoordinate monobutyltin triacetate shows no significant activity as a catalyst, presumably again because it has no tendency to coordinate to the butyl propionate. Its polymeric intermediate hydrolysis product, $[BuSn(O)OCOMe]_n$, is also inactive. It is of interest to compare the organotin trichlorides with monobutyltin tris(triphenylsiloxide), $BuSn(OSiPh_3)_3$, which is sterically hindered from further coordination due to the bulky triphenylsiloxy substituents, and shows no catalytic effect under the conditions used, and with $BuSn(OH)_2Cl$, the activity of which is about one-third that of $BuSnCl_3$, consistent with replacement of two of the chloride groups by hydroxyl radicals.

A study of the transesterification behaviour with methanol of (2-carboalkoxyethyl)tin compounds in which the ester function and tin atom are present in the same molecule has been carried out and the results are summarized in Table 2.

Intramolecular coordination of the carbonyl group in the starting material may be readily determined by the position of the infrared antisymmetric carbonyl stretching vibration, $\nu_{as}(CO)$.[16] As mentioned earlier, the trichloride $BuOCOCH_2CH_2SnCl_3$, in which the carbonyl group is intramolecularly coordinated to the tin atom, undergoes complete transesterification in methanol, whereas the compounds, $BuOCOCH_2CH_2SnBu_3$ and $K_2[BuOCOCH_2CH_2SnF_5]$, which contain free carbonyl groups, do not react with the alcohol. Interestingly, the chloro- and mixed chloro-complexes, in which the carbonyl group is not coodinated to tin, also undergo methanolysis and this may be due to their partial dissociation in refluxing methanol to liberate the free trichloride, which is itself a very active catalyst.

The observed decomposition of the sulphur-containing derivatives (Table 2) could indicate the possibility of reaction at certain labile Sn–X sites to form alkoxides, which then undergo exchange reactions[10] and thereby effect catalysis. In support of this hypothesis, it was found by ^1H NMR spectroscopy that alkoxy exchange does occur in the following reaction (Eqn [7]).

$$BuSn(OMe)Cl_2 + EtCOOBu \rightleftharpoons BuSn(OBu)Cl_2 + EtCOOMe \quad [7]$$

Finally, an investigation of one of the most active catalysts, $BuSnCl_3$, in the esterification of propionic acid with butanol (Eqn [8]) has been carried out using 0.4 mol % of the monobutyltin compound (Fig. 2 and Table 3).

$$EtCOOH + BuOH \rightarrow EtCOOBu + H_2O \quad [8]$$

CONCLUSIONS

From the results obtained in this study, it may be concluded that coordination of the carbonyl group in the ester to the tin catalyst is an important factor influencing its activity and, additionally, alkoxide exchange may have a role to play.

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