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## The structure and Lewis acidity of some triorganotin carboxylates

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### Abstract

A series of tributyltin carboxylates and one triphenyltin carboxylate were prepared by reaction of the tin oxide with the appropriate carboxylic acid. The tin-119 chemical shift of each compound in chloroform and, for the solid carboxylates, in the solid state was determined. A comparison of the solution (109–157 ppm) and solid state shifts (–53 to +45 ppm) indicates that the compounds exist primarily as monomeric 4-coordinate species in solution and as 5-coordinate, presumably polymeric species in the solid state. The Lewis acidity of the compounds toward triethylphosphine oxide (TEPO) was determined by recording the  $^{31}\text{P}$  chemical shift in a mixture of the carboxylate and TEPO in toluene as a function of concentration. Predominant 1:1 adduct formation was observed with equilibrium constants ranging from 5 to 320. The magnitude of the constant can be explained by the electronic effects of the substituents surrounding the tin.

### 1. Introduction

Triorganotin carboxylates are known to exist in several forms, depending on the physical state and the nature of the substituents on the tin and the carbonyl group. Monomeric structures can be either 4-coordinate or 5-coordinate with a bidentate carboxylate, whereas polymeric structures generally contain 5-coordinate tin atoms [1]. It is probably a consequence of the intra- and intermolecular coordination in these compounds that their ability to complex to other donor molecules has not been systematically explored. In a continuation of our studies of the Lewis acidity of organotin compounds [2], we have now prepared a series of triorganotin carboxylates, used  $^{119}\text{Sn}$  NMR to determine the structure of the compounds in solution, and have determined the equilibrium constants for 1:1 adduct formation with triethylphosphine oxide, a Lewis base that has served as a model base in many of our previous studies [3].

### 2. Experimental details

The triorganotin carboxylates, except for tributyltin acetate and triphenyltin acetate which were obtained from Alfa, were prepared by reaction of tributyltin

oxide with the appropriate carboxylic acid. Physical and spectroscopic properties agreed with those previously reported [4]. TEPO was obtained commercially and dried *in vacuo*. Toluene was dried over sodium and stored over molecular sieves.

All glassware was oven-dried at 115°C for at least 1 h and all solutions were prepared in a glove bag containing  $\text{P}_2\text{O}_5$ . The methods used for the determination of equilibrium constants have been previously described [2a].  $^{31}\text{P}$  and  $^{119}\text{Sn}$  solution NMR spectra were obtained on a JEOL FX-90Q spectrometer at 36.19 and 33.34 MHz, respectively, with gated decoupling (no NOE). The probe temperature was  $27 \pm 2^\circ\text{C}$ . CPMAS  $^{119}\text{Sn}$  spectra of compounds in the solid state were obtained on a Varian Unity 300 spectrometer at 111.85 MHz using a Doty 7 mm high speed solids probe. Tetraphenyltin was used to establish the Hartman–Hahn conditions. For each compound, spectra were obtained at three different spin speeds (2500–5500 Hz) in order to identify the centre band(s). Triphenyltin chloride (–33, –35 ppm [5]) and tetraphenyltin (130.6 ppm [6]) were used as substitution references. Typical spectral parameters were: contact time = 2 ms; delay time (between pulses) = 10 s.

### 3. Results and discussion

While the Lewis acidity of inorganic and organotin halides is well known and has been the subject of a

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TABLE 1.  $^{119}\text{Sn}$  chemical shifts and equilibrium constants

	$\delta(^{119}\text{Sn})$ soln	$\delta(^{119}\text{Sn})$ solid	$K(1:1)^a$
$\text{Bu}_3\text{SnOCOCH}_3$	123.1	-47, -53	13
$\text{Bu}_3\text{SnOCOCHCl}_2$	156.7	39, 45	$2.9 \times 10^2$
$\text{Bu}_3\text{SnOCOCH}_2\text{CH}_2\text{Ph}$	108.9	-47	5
$\text{Bu}_3\text{SnOCOCPh}_3$	119.4	-	21
$\text{Bu}_3\text{SnOCOC}_6\text{H}_4\text{C}(\text{CH}_3)_3-4$	110.5	0	35
$\text{Bu}_3\text{SnOCOC}_6\text{H}_3(\text{NO}_2)_2-3,5$	144.7	-	$3.2 \times 10^2$
$\text{Ph}_3\text{SnOCOCH}_3$			74

<sup>a</sup>  $\pm 15\%$  for reaction with TEPO in toluene (except triphenyl derivative which was in benzene) at  $27 \pm 2^\circ\text{C}$ .

number of our studies [2], the Lewis acidities of other organotin compounds have received little attention. It is generally assumed that at least one electronegative group is required to confer significant acidity. The oxygen of alkoxides, hydroxides, and carboxylates surely meets the electronegativity requirement. However, all of these derivatives are known to engage in self-association, depending on concentration (or state), solvent, and the nature of the molecule.

For the present investigation we have chosen a series of triorganotin carboxylates. These compounds can exist as monomeric compounds with 4-coordinate tin sites, as monomeric compounds with bidentate carboxylate groups producing a 5-coordinate tin, or as polymeric compounds with bridging carboxylate groups that generally produce 5-coordinate tin sites. Although the polymeric structure is favored for most compounds in the solid state, studies of triorganotin carboxylates indicate that most exist as monomeric 4-coordinate species in non-coordinating solvents [7,8].

The tin-119 chemical shift data in Table 1 confirm the hypothesis that the compounds studied exist in solution as monomeric 4-coordinate species. The shifts in solution range from 109 to 157 ppm relative to tetramethylstannane, similar to the range of shifts previously observed for 4-coordinate tributyltin derivatives [7], with an apparent dependence on the effective electronegativity of the group attached to the carbonyl carbon (the largest shifts occur for the dichloroacetate and 3,5-dinitrobenzoate derivatives). Predominance of the monomeric species in solution is also corroborated by the  $^{119}\text{Sn}$  shift of tributyltin acetate, which has been found to vary only slightly (several ppm) with a change in concentration in  $\text{CDCl}_3$  [7]. The solution shifts in  $\text{CDCl}_3$  agreed within 5 ppm to those reported previously [4,7] with the exception of two compounds,  $\text{Bu}_3\text{SnOCOCH}_2\text{CH}_2\text{Ph}$  (lit. [4], 96.5 ppm) and  $\text{Bu}_3\text{SnOCOCH}_3$  (lit. [7], 106.9 ppm). Although some difference in shift can be expected because of the different

concentrations and temperatures employed, we have no explanation for the discrepancy of 13 and 17 ppm, respectively, observed for these two compounds.

The shifts of several of the solid carboxylates in the solid state further substantiate the structure of the compounds in solution. These solid state values are 100–180 ppm to lower frequencies than the solution values, again in accord with previous observations about the effect of a change from 4- to 5-coordination [7,8]. The two isotropic shifts for the acetate have been attributed to two different environments for tin in the crystal lattice [9]; the same phenomena can also be seen for the dichloroacetate.

The Lewis acidity of the compounds toward TEPO in toluene were determined by observing the  $^{31}\text{P}$  chemical shift as a function of concentration for 1:1 mixtures of the carboxylates with TEPO. The plot of the  $^{31}\text{P}$  chemical shift as a function of  $(\text{shift}/\text{conc})^{1/2}$  should produce a straight line if only a 1:1 adduct is formed. In fact the plots for most of the compounds are good straight lines (see ref. [2c]) with correlation coefficients of 0.97 to 0.99. The plots for the 3-phenylpropanoate and the acetate exhibit definite curvature attributable to the presence of a second equilibrium. The values for the equilibrium constants for the 1:1 adducts were determined as described previously [2] and are given in Table 1. The constants for the 3-phenylpropanoate and acetate derivatives must be considered to be less accurate than those for the other derivatives.

The dependence of the constants on electronic effects is clear from the data in Table 1; the largest constants are produced by the electron-withdrawing dichloroacetate and 3,5-dinitrobenzoate groups. The constant for triphenyl acetate reveals that the electronic effect is also important for groups attached directly to the tin. The lack of a significant steric effect shown by a comparison of tributyltin acetate with tributyltin triphenylacetate is not altogether surprising in view of the distance of the bulk from the acidic site.

Finally, a comparison of the constants for triphenyltin chloride ( $1.7 \times 10^2$  in benzene [3]) and triphenyltin acetate (74 in toluene) indicates the relative ability of the two groups to increase the acidity of the tin site.

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