

Preliminary communication

^{119}Sn chemical shifts in organotin carboxylates

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SUMMARY

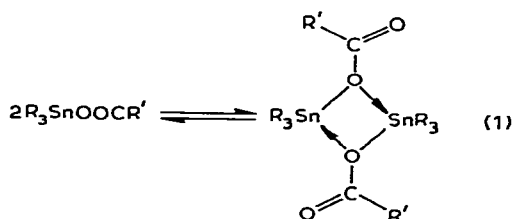
^{119}Sn chemical shifts determined by heteronuclear magnetic double resonance in $\text{Nph}_3\text{SnOOCR}^*$ and Ph_3SnOOCR are linearly related to the $\text{p}K_a$ of RCOOH . It appears that the greater polarizability of tin leads to a greater sensitivity to changes in electronic environment than in similar silicon and carbon compounds.

With one exception¹, studies of ^{119}Sn chemical shifts aimed at establishing correlations with structural and electronic features have used molecules of widely divergent types²⁻⁶. In these circumstances it is difficult to know which changes are responsible for the observed variations in the tin shielding, so we have now examined some organotin derivatives of carboxylic acids in which the electron-withdrawing ability of the carboxylate group can be assessed from the $\text{p}K_a$ of the parent acid. For a series of compounds $\text{R}_3\text{SnOOCR}'$ in which only R' is varied, the point of variation is three bonds removed from the tin atom, and it is reasonable to suppose that extraneous factors such as changes in dispersion forces and electric field effects will be negligible at the tin atom. The change in the tin shielding will then arise directly from an alteration in the amount of inductive electron withdrawal by the carboxylate group.

Many triorganotin carboxylates with small alkyl groups attached to tin form dimers in which the ^{119}Sn chemical shift is ca. 100 ppm to high field of that in the monomeric species, and in solution there is an equilibrium (1) so that the observed tin shielding reflects the relative proportions of monomer and dimer as well as the electron withdrawing ability of the carboxylate group⁷. For example, the ^{119}Sn chemical shift of trimethyltin formate is +2.5 ppm in 3*M* deuteriochloroform solution, and changes

* $\text{Nph} = \text{Me}_2\text{PhCCH}_2$

monotonically to +150 ppm on dilution to 0.05M in the same solvent. However, such equilibria do not appear to be important for solutions of the bulkier trialkyl- and triaryltin carboxylates, and the ^{119}Sn chemical shifts of these are essentially independent of concentration.



In the present work heteronuclear $^1\text{H}-\{^{119}\text{Sn}\}$ double resonance experiments⁸ have been used to determine ^{119}Sn chemical shifts in a number of trineophyl- \star and triphenyltin carboxylates in dilute [$< 0.5M$] solution. In a typical experiment the ^{119}Sn satellites of the neophylmethylene proton resonance [$^2J(^{119}\text{Sn}\cdots\text{H}) = 49.5 \text{ Hz}$] or of the *ortho*-phenyl proton resonance [$^3J(^{119}\text{Sn}\cdots\text{H}) = \text{ca. } 55 \text{ Hz}$] were observed while the sample was simultaneously irradiated at the tin resonance frequency (22.37 MHz). All spectra were recorded at a proton frequency of 60 MHz using samples which contained ^{119}Sn ($I = 1/2$) in natural abundance (8.7%).

The results are given in Table 1 and are plotted against the $\text{p}K_a$ of the parent acid in Fig. 1. It is clear that increased inductive electron withdrawal from tin gives shifts to low field, with gradients of 15 and 14.5 ppm per $\text{p}K_a$ unit respectively for the two series.

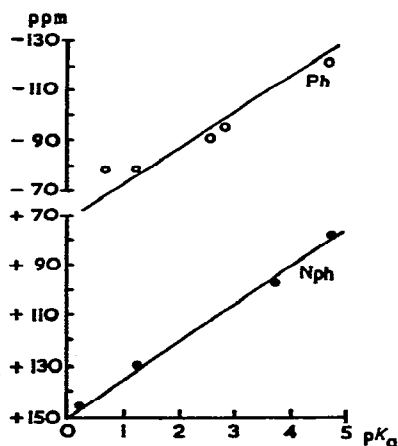


Fig. 1. ^{119}Sn chemical shifts in ppm to low field of $(\text{CH}_3)_4\text{Sn}$ in $[(\text{CH}_3)_2\text{C}_6\text{H}_5\text{CCH}_2]_3\text{SnOOCR}$ and $(\text{C}_6\text{H}_5)_3\text{SnOOCR}$ vs. the $\text{p}K_a$ of RCOOH .

\star Neophyl = $\text{Me}_2\text{PhCCH}_2$ (Nph).

TABLE 1

¹¹⁹Sn CHEMICAL SHIFTS IN ORGANOTIN CARBOXYLATES

Compound	<i>pK_a</i> of parent acid	Ξ (¹¹⁹ Sn) in Hz ^a	δ(¹¹⁹ Sn) ^b
Nph ₃ SnOOCMe ^c	4.76	37,293,610	+79
Nph ₃ SnOOCH	3.75	37,294,320	+98
Nph ₃ SnOOCCHCl ₂	1.23	37,295,550	+131
Nph ₃ SnOOCF ₃	0.22	37,296,110	+146
Nph ₃ SnF		37,295,850	+139
Nph ₃ SnCl		37,295,070	+118
Nph ₃ SnOH		37,296,670	+161
Ph ₃ SnOOCMe	4.76	37,286,150	-121
Ph ₃ SnOOCCH ₂ Cl	2.86	37,287,120	-95
Ph ₃ SnOOCCH ₂ F	2.58	37,287,310	-90
Ph ₃ SnOOCCH ₂ Me	4.87	37,286,150	-121
Ph ₃ SnOOCCHCl ₂	1.23	37,287,720	-79
Ph ₃ SnOOCCL ₃	0.66	37,287,680	-80
Ph ₃ SnCl		37,288,870	-48
Ph ₃ SnOH		37,287,460	-86

^aResonance frequency in a field in which TMS gives a proton resonance of 100 MHz. ^bTo low field of Me₄Sn. ^cNph = Me₂PhCCH₂.

There is evidence that the relatively high field ¹¹⁹Sn chemical shifts found for triphenyltin derivatives in general arise because of π-back bonding between the aromatic system and the vacant tin 5*d* orbitals⁶.

It is generally accepted that tin shielding will be dominated by the paramagnetic contribution given by equation (2)⁹.

$$\sigma_{para} = \frac{A}{\Delta E} \left\{ \langle r_{5p}^{-3} \rangle Q_{5p} + \langle r_{5d}^{-3} \rangle Q_{5d} \right\} \dots \quad (2)$$

where Δ*E* is a mean excitation energy which may be regarded as constant within a series of closely related compounds, ⟨*r*_{5*p*}⁻³⟩ and ⟨*r*_{5*d*}⁻³⟩ are the mean inverse cubes of the valence *p* and *d* electron radii, and the *Q*'s are related to the electron imbalance in the bonds to tin. *A* is a constant. An increase in the electronegativity of a substituent will increase *Q* and so will give a shift to low field. Studies of analogous silicon compounds have shown that *Q*_{3*d*} is relatively unimportant, and that the changes in the silicon shielding are dominated by variations of *Q*_{3*p*} as the carboxylate group is altered¹⁰. If a similar situation holds for the tin compounds the gradients of the plots of δ(²⁹Si) and δ(¹¹⁹Sn) vs. *pK_a* should be proportional to ⟨*r*_{3*p*}⁻³(Si)⟩ and ⟨*r*_{3*p*}⁻³(Sn)⟩ respectively, provided that the mean excitation energies are comparable, as seems likely. For the three series of comparable compounds ROOCCH₃¹¹, ROOCSiMe₃¹⁰, and ROOCNph₃ the gradients of the plots of δ(¹³C), δ(²⁹Si) and δ(¹¹⁹Sn) vs. the *pK_a* of RCOOH are 0.75, 2.0, and 15.0 ppm/*pK_a* unit respectively, while the corresponding values of ⟨*r*_{*np*}⁻³⟩ are in the approximate ratios 1/1.3/3.8. That is, factors of 2.1 and 2.5 remain unaccounted for in going from

carbon to silicon, and from silicon to tin. Thus it appears that the magnetic shielding of the nuclei of the heavier atoms is more sensitive to changes in electronic environment, and it is reasonable to attribute this to the greater polarizability of these atoms.

For the trineophyl compounds the tin chemical shifts of the fluoride and chloride are as would be expected on electronegativity grounds, but the position of the hydroxide appears to be anomalous. For the triphenyl series however, the chloride has a tin chemical shift which is outside the range of the carboxylates and this may reflect π -interactions involving the tin $5d$ and chlorine $3p$ atomic and the aromatic molecular orbitals.

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