Heteroatom Chemistry
Volume 7, Number 1, 1996

Structures and Relationship between the ^{119}Sn NMR Chemical Shifts and pK_a of Their Parent Acids in Organotin(IV) Carboxylates

Zhengkun Yu* and Shihua Wang

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China

Shenggang Yan

Laboratory of Organic Chemistry, College of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

Received 2 May 1995; revised 23 June 1995

ABSTRACT

Ten di-n-butyltin(IV) carboxylates $[(^{n}Bu_2SnOCOR')_2O]_2$ *and* $^{n}Bu_2Sn(OCOR')_2$ *(R′ =* CCl_3, $CHCl_2$, CH_2Cl, *PhCH=CH, and 2,2,3,3-tetramethylcyclopropyl) were synthesized and characterized by IR,* ^{1}H, ^{13}C, ^{119}Sn *NMR spectroscopy and elemental analysis. Together with other series of organotin(IV) carboxylates, their structural features were discussed. The relationship between the* ^{119}Sn *NMR chemical shifts in the organotin(IV) carboxylates* $[(^{n}Bu_2SnOCOR')_2O]_2$, $^{n}Bu_2Sn(OCOR')_2$, $^{n}Bu_3SnOCOR'$, $Ph_3SnOCOR'$ *and the p*K_a *values of their parent acids R′COOH was studied. The results have shown that the log[-δ(*^{119}Sn*)] of the same series of carboxylates is linearly related to the p*K_a *of R′COOH. It seems that the better is the linearity between the log[-δ(*^{119}Sn*)] and the p*K_a*, the more analogous are the structures of the same series of carboxylates.*

INTRODUCTION

The study of the structural chemistry of organotin(IV) compounds has received considerable attention owing to the various structural types in which some series of organotin(IV) carboxylates can be used as biocidally active reagents [1,2] and homogeneous catalysts [3]. The ^{119}Sn NMR spectra of organotin(IV) compounds in solutions have provided very important information in determination of their structures [4–6]. McFarlane and Wood [7] reported that the $\delta(^{119}Sn)$ of several kinds of $Nph_3SnOCOR'$ ($Nph = Me_2PhCCH_2$) and $Ph_3SnOCOR'$ are linearly related to the pK_a values of the respective R′COOH, and Xie et al. [8] discussed the linear free energy relationship between the $\delta(^{119}Sn)$ in some $(PhMe_2SiCH_2)_3SnOCOR'$ and the parasubstituent constants σ of their parent aromatic acids, but these linear relationships were only used in a limited range of the same series of organotin(IV) compounds. In this article, we carried out a first study on the relationship between the log[$-\delta(^{119}Sn)$] and the pK_a of their parent acids R′COOH in di-n-butyl tetraorganotin(IV) and diorganotin(IV), tri-n-butyltin(IV), and triphenyltin(IV) carboxylates: $[(^{n}Bu_2SnOCOR')_2O]_2$, $^{n}Bu_2Sn(OCOR')_2$, $^{n}Bu_3SnOCOR'$, and $Ph_3SnOCOR'$. The results have shown that the log[$-\delta(^{119}Sn)$] of the organotin(IV) carboxylates in which other ligating atoms except the oxygen atoms of the carboxylate groups cannot coordinate to the central tin atoms is linearly related to the pK_a of R′COOH. The linearity and the linearity range between the log[$-\delta(^{119}Sn)$] and pK_a of R′COOH are

---

*To whom correspondence should be addressed.

1042-7163/96/010003-06

TABLE 1 The Physical Properties and Analytical Data of Di-n-butyltin(IV) Carboxylates

No. Carboxylate	*M.p. (°C)*	*Solvent*^{a}	*Yield (%)*	*Anal. [Found (Calcd.)] (%)*		
				C	*H*	*Sn*
A1 $[(^{n}Bu_2SnOCOCCl_3)_2O]_2$	166	ethanol	80	30.01 (29.79)	4.60 (4.46)	29.30 (29.44)
A2 $[(^{n}Bu_2SnOCOCHCl_2)_2O)]_2$	193	ethanol	73	33.02 (32.58)	5.34 (5.15)	32.21 (32.19)
A3 $[(^{n}Bu_2SnOCOCH_2Cl)_2O]_2$	87	ethanol	73	36.18 (35.93)	6.25 (5.98)	35.36 (35.51)
A4 $[(^{n}Bu_2SnOCOCH=CHPh)_2O]_2$	59	ethanol/benzene (1/1)	74	52.66 (52.62)	6.41 (6.54)	31.09 (30.62)
A5 $[(^{n}Bu_2SnOCOCH(C)_2(CH_3)_4)_2O]_2$	101	ethanol/benzene (1/1)	85	49.63 (50.32)	8.10 (8.12)	31.46 (31.08)
B1 $^{n}Bu_2Sn(OCOCCl_3)_2$	99	ethanol	78	25.60 (25.83)	3.18 (3.23)	21.34 (21.29)
B2 $^{n}Bu_2Sn(OCOCHCl_2)_2$	96	ethanol	84	29.60 (29.50)	4.25 (4.09)	24.18 (24.29)
B3 $^{n}Bu_2Sn(OCOCH_2Cl)_2$	140	ethanol	81	34.62 (34.34)	5.34 (5.24)	28.43 (28.28)
B4 $^{n}Bu_2Sn(OCOCH=CHPh)_2$	71	ethanol/benzene (1/1)	73	60.13 (59.24)	6.09 (6.08)	22.28 (22.54)
B5 $^{n}Bu_2Sn(OCOCH(C)_2(CH_3)_4)_2$	36	ethanol/benzene (1/1)	85	55.95 (55.98)	8.41 (8.54)	22.90 (23.05)

[a] Solvent of recrystallization.

much better than those between the $\delta(^{119}Sn)$ and the pK_a (or σ) reported in the literature [7,8].

RESULTS AND DISCUSSION

Characterization of Organotin(IV) Carboxylates A1–A5 *and* B1–B5 *(Table 1)*

The IR spectra imply the presence of bidentate and chelating carboxylate groups, with $\Delta\nu = [\nu(OCO)_{asym} - \nu(OCO)_{sym}]$ of greater than 200 cm^{-1}. The Sn–C absorption in the region of 465–505 cm^{-1} reveals a *trans* configuration of the $^{n}Bu_2Sn$ moiety [5]. A band in the region of 484–616 cm^{-1} is assigned to the stretching mode of the Sn–O linkage. In the case of the 1:1 carboxylates $[(^{n}Bu_2SnOCOR')_2O]_2$, a strong band in the region 606–638 cm^{-1} is attributed to ν(Sn–O–Sn), which indicates an Sn–O–Sn bridged structure for these carboxylates. The presence of two values for $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ in the case of 1:1 carboxylates means that the two carboxylate groups are asymmetrically bonded in the carboxylates [9].

The $\delta(\alpha$–H) of the carboxylate groups in ^{1}H NMR spectra is shifted upfield compared with that of the parent acid, which indicates that the α-H in the carboxylate groups is shielded more than in the free acids, and the oxygen atoms of the carboxylate groups cannot only bind, but also coordinate to the central tin atoms. The ^{13}C NMR spectra of carboxylates **B1–B5** and **A1–A5** (Table 2) displayed one and two sets of Sn–^{n}Bu resonances, respectively. Ligand carbons in all cases appeared as singlets. The ^{119}Sn NMR spectra of **B1–B5** (Table 3) displayed single resonances in the region δ −149.2 to −189.8; in contrast the ^{119}Sn NMR spectra of **A1–A5** exhibited two signals in the region δ −165.2 to −223.1. According to Holecek et al.'s suggestion [4], the central tin atoms can be assigned to be five- and/or six-coordinate. The ^{13}C and ^{119}Sn NMR data for the carboxylates **A1–A5** are consistent with a dimeric tetraorganostannoxane structure [10]. Only single resonances were observed for OCO groups in the ^{13}C spectra due to either accidental magnetic equivalence of the carbonyl carbon atoms or to a dynamic equilibrium between possible isomeric structures [11].

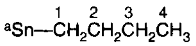
According to the spectral features of these carboxylates and the crystal structure of **A1** [12], the structures of these carboxylates were inferred as follows. Compounds **A2–A5** feature a central Sn_2O_2 unit and two other Sn atoms coordinated by the bridging oxygen atoms. A further link between the exocyclic and endocyclic Sn atoms is provided by two bridging carboxylate ligands. Compounds **B1–B5** feature the typical structures of diorganotin(IV) carboxylates.

Dimeric Di-n-butyltin(IV) Carboxylates

Carboxylates $[(^{n}Bu_2SnOCOR')_2O]_2$ exhibit two sets of ^{119}Sn resonances in solution, which means that they are present as dimers [5,10,12]. It is known from the reported structures, determined by IR, NMR spec-

TABLE 2 The ^{13}C NMR Chemical Shifts of Carboxylates **A1–A5** and **B1–B5**

No.	*δ(^{13}C) (ppm)*^{a}
A1	165.30(OCO), 93.00(CCl_3), 27.57(C1), 27.04, 26.98(C2), 26.88(C3), 13.48(C4)
A2	169.03(OCO), 66.75($CHCl_2$), 30.44(C1), 27.93, 27.56(C2), 27.05, 26.64(C3), 13.47(C4)
A3	172.31(OCO), 42.45(CH_2Cl), 30.01, 29.61(C1), 27.50, 27.02(C2), 26.56, 26.09(C3), 13.41(C4)
A4	172.72(OCO), 143.58(C8′), 134.88(C1′), 129.76(C4′), 128.76(C3′, C5′), 127.86(C2′, C6′), 121.39(C7′), 29.07, 29.00(C1), 27.64, 27.37(C2), 26.81(C3), 13.61(C4)
A5	178.30(OCO), 38.10(CH), 29.09(tertiary carbon), 27.29(C1), 27.02, 26.91(C2), 26.67, 26.59(C3), 23.74(2 × CH_3 of cyclopropyl), 16.80(2 × CH_3 of cyclopropyl), 13.55(C4)
B1	168.63(OCO), 90.84(CCl_3), 27.08(C1), 26.49(C2), 26.15(C3), 13.36(C4)
B2	168.76(OCO), 66.85($CHCl_2$), 27.51(C1), 27.02(C2), 26.63(C3), 13.42(C4)
B3	171.97(OCO), 42.66(CH_2Cl), 27.43(C1), 27.07(C2), 26.63(C3), 13.45(C4)
B4	175.62(OCO), 146.15(C8′), 134.28(C1′), 130.23(C4′), 128.74(C3′, C5′), 128.03(C2′, C6′), 117.62(C7′), 26.51(C1), 26.18(C2), 25.20(C3), 13.35(C4)
B5	182.74(OCO), 36.30(CH), 30.22(tertiary carbon), 26.64(C1), 26.16(C2), 24.77(C3), 23.52(2 × CH_3 of cyclopropyl), 16.80(2 × CH_3 of cyclopropyl), 13.44(C4)



$^{a}Sn{-}\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3$

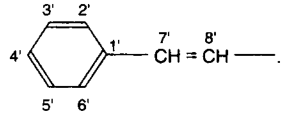


TABLE 3 The δ(^{119}Sn) and the pK_a of Their Parent Acids in Di-n-butyltin(IV) Carboxylates

No.	*Carboxylate*	*δ(^{119}Sn)*	*(ppm)*	*pK_a*^{a}	*Ref.*
A1	$[(^nBu_2SnOCOCCl_3)_2O]_2$	−165.2	−189.4	0.66	this work
A2	$[(^nBu_2SnOCOCHCl_2)_2O]_2$	−189.4	−190.4	1.25	this work
A3	$[(^nBu_2SnOCOCH_2Cl)_2O]_2$	−197.0	−206.6	2.86	this work
A4	$[(^nBu_2SnOCOCH{=}CHPh)_2O]_2$	−202.3	−214.8	5.55	this work
A5	$[(^nBu_2SnOCOCH(C)_2(CH_3)_4)_2O]_2$	−203.7	−223.1	6.81	this work
A6	$[(^nBu_2SnOCOC_4H_3O)_2O]_2$	−194.1	−222.4	3.16	[5]
A7	$[(^nBu_2SnOCOC_4H_3S)_2O]_2$	−208.4	−210.4	3.53	[5]
A8	$[(^nBu_2SnOCOC_6H_4OMe{-}2)_2]_2$	−199	−203	4.08	[10]
A9	$[(^nBu_2SnOCOC_5H_4N)_2O]_2$	−229.8	−269.0	1.01	[13]
B1	$^nBu_2Sn(OCOCCl_3)_2$	−180.0		0.66	this work
B2	$^nBu_2Sn(OCOCHCl_2)_2$	−189.8		1.25	this work
B3	$^nBu_2Sn(OCOCH_2Cl)_2$	−196.2		2.86	this work
B4	$^nBu_2Sn(OCOCH{=}CHPh)_2$	−149.2		5.55	this work
B5	$^nBu_2Sn(OCOCH(C)_2(CH_3)_4)_2$	−154.0		6.81	this work
B6	$^nBu_2Sn(OCOMe)_2$	−149.3		4.75	[4]
B7	$^nBu_2Sn(OCOPh)_2$	−149.9		4.2	[4]
B8	$^nBu_2Sn(OCOC_6H_4OMe{-}2)_2$	−149		4.08	[10]

[a] pK_a values are obtained from the literature cited in column 5 or from *Lange's Handbook of Chemistry* (13th ed., edited by J. A. Eean, McGraw-Hill Book Company, 1985).

troscopy, and X-ray analyses, that their structures in solution are analogous to those in the solid state; that is, the tetraorganostannoxane structures with six-coordination (or five-coordination in some cases) assigned to the endocyclic and exocyclic tin atoms [12,13]. In Figure 1a, two approximately parallel straight lines are obtained. The ^{119}Sn chemical shifts observed at low field (datum spot, ○) and at high field (datum spot, ●) are attributed to the exocyclic and endocyclic Sn atoms, respectively. It has been confirmed by X-ray diffraction studies that the tin atoms corresponding to the datum spots found correctly on the straight lines are usually six-coordinate [5,10,12]. The datum spots for the central tin atoms with the analogous structures (or the same coordination numbers) lie on the same straight line. The high-field datum spot of **A1** (δ(^{119}Sn) = δ −165.2) corresponding to a five-coordinate tin center, which has been confirmed by an X-ray analysis [12], shows obvious displacement from the straight line for the high-field shifts, but its low-field datum spot (-δ(^{119}Sn) = −189.4) correctly lies on the straight line for the low-field shifts. When there is a nonoxygen atom of the carboxylate group participating in the coordination to tin, for example, in compound **A9** $[(^nBu_2SnOCOC_5H_4N)_2O]_2$, the nitrogen atoms can

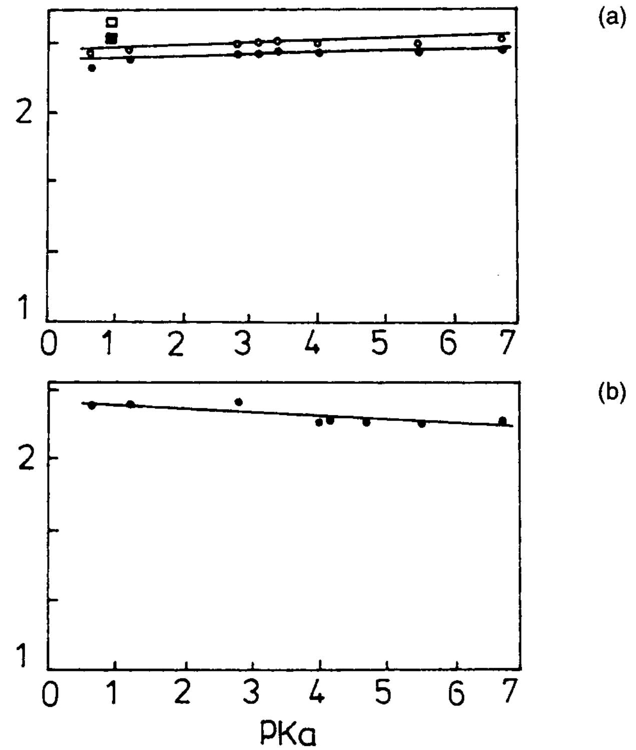


FIGURE 1 The log[-δ(^{119}Sn)] vs. the pK_a of their parent acids R'COOH in di-n-butyltin(IV) carboxylates $[(^nBu_2Sn\text{-}OCOR')_2O]_2$ and $^nBu_2Sn(OCOR')_2$. (a) $[(^nBu_2SnOCOR')_2O]_2$: ○, ^{119}Sn resonances at low field; ●, ^{119}Sn resonances at high field; □, ■, compound **A9**. (b) $^nBu_2Sn(OCOR')_2$.

coordinate to the central tin atoms, among which one tin atom is six-coordinate and the other is seven-coordinate [13]. The two types of environments for tin atoms can be described as being based on distorted octahedral and pentagonal bipyramidal geometries that are different from those of dicarboxylato tetraorganostannoxanes. Its datum spots (■ and □) are displaced considerably from the approximately parallel straight lines.

Di-n-butyltin(IV) Dicarboxylates

According to the studies of Holecek et al. [4], carboxylates **B1** and **B4–B8** are typical of a five-coordinate tin structure (δ(^{119}Sn) = −149.2 to −180.0). In solution, an intramolecular exchange [14] and a rapid bidentate-unidentate interchange of the coordinating groups [15] may be present. The higher Lewis acidity of the $^nBu_2Sn$ moiety than that of the $^nBu_3Sn$ moiety results in a stronger coordination bond (Sn ⋯ O–C) in this series of carboxylates than that in tri-n-butyltin(IV) derivatives [14].

The log[-δ(^{119}Sn)] of these compounds is linearly related to the pK_a of R'COOH (Figure 1b). For carboxylate **B2**, its chemical shift (δ −189.8) being on the edge of the δ(^{119}Sn) range suggested for a five-coordinate di-n-butyltin(IV) compound (δ −190 to −90) by Holecek et al. [4], it may be a five- or six-coordinate compound. It can be seen from Figure 1b that its datum spot correctly lies on the straight line for the five-coordinate tin atoms, so it is reasonable to attribute its tin atom to be five-coordinate. For carboxylate **B3**, its δ(^{119}Sn) (−196.2) being out of the δ(^{119}Sn) range suggested for a four- or five-coordinate di-n-butyltin(IV) compound, it may have a six-coordinate central tin atom according to the obvious displacement of its datum spot from the straight line for the five-coordinate carboxylates.

Tri-n-butyltin(IV) Carboxylates

The data of carboxylates **C1–C7** (Table 4) reveal that this series of triorganotin(IV) carboxylates exist as monomeric species in solution. Their chemical shifts range from δ −104.8 to −156.7 relative to Me_4Sn, similar to the range of the shifts previously observed for other four-coordinate tri-butyltin(IV) derivatives [16], with an apparent dependence on the effective electronegativity and a relatively small dependence on the steric effect of the group attached to the carbonyl carbon (the largest shifts occurring for the dichloroacetate and 3,5-dinitrobenzoate derivatives).

Lycka and Holecek [14] have confirmed this series of organotin carboxylates to be four-coordinate, in spite of the presence of an intramolecular exchange observed by ^{17}O NMR technique in solution, although the crystallographic evidence shows that most triorganotin(IV) alkonates are generally five-coordinate, carboxylate-bridged polymers in the solid state [17]. The coordination of oxygen atoms of the carbonyl groups to the central tin atoms is relatively weak, and the geometry differs only slightly from the tetrahedral arrangement of compounds containing four-coordinate tin atoms [18,19]. From Figure 2a, it can be seen that the log[-δ(^{119}Sn)] of these tri-n-butyltin(IV) carboxylates linearly decreases as the pK_a values of their parent acids increase (slope < 0), which indicates that their structures in solution are very analogous.

Triphenyltin(IV) Carboxylates

Molloy et al. [6] have confirmed that compounds **D1–D10** have the constant four-coordinate structures in solution and in the solid state by IR and ^{119}Sn Mössbauer spectroscopy. The data suggest that this series of carboxylates are tetrahedral at tin in solution or in the solid state, and that chelation by the carboxylate group to form the *cis*-SnR_3O_2 structure

TABLE 4 The $\delta(^{119}Sn)$ and the pK_a of Their Parent Acids in Triorganotin(IV) Carboxylates $R_3SnOCOR'$ (R = ^nBu, Ph)

No.	*Carboxylate*	*$\delta(^{119}Sn)(ppm)$*	*pK_a*	*Ref.*
C1	$^nBu_3SnOCOPh$	−112.7	4.20	[16]
C2	$^nBu_3SnOCOMe$	−104.8	4.75	[16]
C3	$^nBu_3SnOCOCHCl_2$	−156.7	1.25	[22]
C4	$^nBu_3SnOCOCH_2CH_2Ph$	−108.9	4.66	[22]
C5	$^nBu_3SnOCOCPh_3$	−119.4	3.96	[22]
C6	$^nBu_3SnOCOC_6H_4C(Me)_3$–4	−110.5	4.2	[22]
C7	$^nBu_3SnOCOC_6H_3(NO_2)_2$–3,5	−144.7	2.85	[22]
D1	$Ph_3SnOCOPh$	−114.3	4.20	[6]
D2	$Ph_3SnOCOC_6H_4NH_2$–2	−119.5	4.91	[6]
D3	$Ph_3SnOCOC_6H_4Me$–2	−119.9	3.91	[6]
D4	$Ph_3SnOCOC_6H_4OMe$–2	−121.9	4.08	[6]
D5	$Ph_3SnOCOC_6H_4F$–2	−108.9	3.27	[6]
D6	$Ph_3SnOCOC_6H_4Cl$–3	−105.9	3.83	[6]
D7	$Ph_3SnOCOC_6H_3Cl_2$–2,5	−99.5	2.55	[6]
D8	$Ph_3SnOCOC_6H_3Cl_2$–3,4	−103.0	3.59	[6]
D9	$Ph_3SnOCOC_6H_4NO_2$–3	−97.9	3.46	[6]
D10	$Ph_3SnOCOC_6H_3(NO_2)_2$–3,5	−84.9	2.72	[6]
D11	$Ph_3SnOCOC_6H_3Cl_2$–2,6 · .5C_6H_{12}	−93.0	1.64	[6]
D12	$Ph_3SnOCOC_6H_3Cl_2$–2,3 · 0.5Me_2CO	−100.6	2.55	[6]
D13	$Ph_3SnOCOC_6H_4NO_2$–2	−92.8	2.21	[6]
D14	$Ph_3SnOCOC_6H_3Cl_2$–2,4	−102.1	2.68	[6]
D15	$Ph_3SnOCOC_6H_4Br$–2	−105.9	2.85	[6]
D16	$Ph_3SnOCOC_6H_4Cl$–2	−107.9	2.92	[6]
D17	$Ph_3SnOCOMe$	−121	4.75	[7]
D18	$Ph_3SnOCOCH_2C1$	−95	2.86	[7]
D19	$Ph_3SnOCOCH_2F$	−90	2.85	[7]
D20	$Ph_3SnOCOCH_2Me$	−121	4.87	[7]
D21	$Ph_3SnOCOCHCl_2$	−79	1.25	[7]
D22	$Ph_3SnOCOCCl_3$	−80	0.66	[7]

is absent or very weak [14,18,20]. The structure of four-coordinate triorganotin(IV) carboxylate has also been determined by X-ray diffraction; for example, in the solid state $Ph_3Sn(O_2CC_4H_3S)$ is monomeric with a four-coordinate tin atom [21]. Although carboxylates **D11–D16** are present in the polymeric state in the solid state [6,20], this polymeric structure is disrupted upon dissolution to yield tetrahedral monomers ($\delta(^{119}Sn) = -92.8$ to -107.9). In Figure 2b, the $\log[-\delta(^{119}Sn)]$ of the triphenyltin(IV) benzoates is linearly related to the pK_a of R'COOH (data spots, ●). The positive slope means that the stronger electronic factor (smaller pK_a) lessens the intramolecular exchange analogous to that in tri-n-butyltin(IV) carboxylates, and thus triphenyltin(IV) carboxylates with larger pK_a values for their parent acids show their ^{119}Sn resonances at relatively low field. It can also be seen from Table 4 that the derivatives of aliphatic acids **D17–D22** exist as tetrahedral monomers in solution. Their $\log[-\delta(^{119}Sn)]$ is linearly related to the pK_a of R'COOH (data spots, ○), and the linearity (between $\log[-\delta(^{119}Sn)]$ and pK_a) is much better than that between $\delta(^{119}Sn)$ and pK_a [7].

The different slopes for the two straight lines of triorganotin(IV) carboxylates shown in Figure 2 reflect different electronic and steric influences for the alkyl groups attached to the central tin atoms [22]. When the group attached to the carbonyl carbon is less electronegative (large pK_a), the electron-withdrawing ability of a R'COO moiety is decreased, and the electron-donoring ability (coordinating ability) of the carbonyl oxygen atom increases. In tri-n-butyltin(IV) derivatives, the relatively weak Lewis acidity of $^nBu_3Sn$ or $^nBu_3SnOCOR'$ gradually decreases as the pK_a increases, and an increase of electron density on the tin atom of the $^nBu_3Sn$ moiety may hinder the intramolecular exchange; thus the coordination of carboxylate groups to tin atoms is gradually weakened as the pK_a increases, and the ^{119}Sn resonances gradually appear at the higher field (slope < 0). For the triphenyltin(IV) derivatives, the shielding for tin atoms is dominated by the paramagnetic contribution from its 5*p* orbitals [7,23]. The hyperconjugation between the 5*p* orbitals of tin atoms and the π orbitals of the phenyl groups leads to an increase of the Lewis acidity of $Ph_3SnOCOR'$ (that is, the tin atom becomes more electronically positive) and then promotes the previously mentioned intramolecular exchange.

According to the discussion about the relationship between the $\log[-\delta(^{119}Sn)]$ of the preceding four series of organotin(IV) carboxylates and the pK_a of

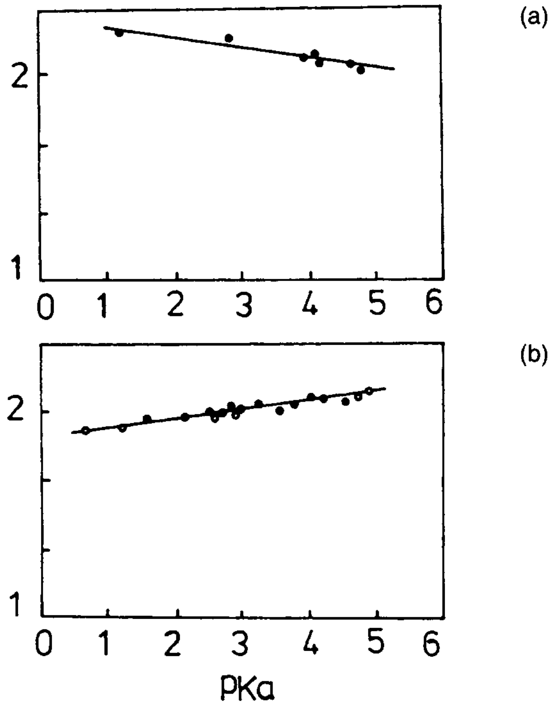


FIGURE 2 The log[-$\delta(^{119}Sn)$] vs. the pK_a of their parent acids R′COOH in triorganotin(IV) carboxylates $^nBu_3SnOCOR'$ and $Ph_3SnOCOR'$. (a) $^nBu_3SnOCOR'$. (b) $Ph_3SnOCOR'$: ●, R′ = aromatic groups; ○, R′ = alkyl groups.

their parent acids, a conclusion can be drawn that the log[-$\delta(^{119}Sn)$] is linearly related to the pK_a if the same series of organotin(IV) carboxylates containing no other coordinating atoms except the carboxyl oxygen atoms have analogous structures (i.e., the same coordination for tin atoms). The better the linearity, the more analogous are the structures of the same series of organotin(IV) carboxylates.

EXPERIMENTAL

All solvents were used after purification and drying. Other reagents were used as supplied.

Exactly 0.90 g (0.0036 mol) of $^nBu_2SnO$ and 0.60 g (0.0036 mol) of Cl_3CCOOH were added to 40 mL of ethanol-benzene (3/1, v/v) successively. The mixture was stirred under reflux for 4 hours. Water formed during the reaction was removed azeotropically with a Dean and Stark water trap. The clear solution was cooled to room temperature and filtered, and then the solvent was removed under reduced pressure. Pure compound **A1** (1.15 g, yield 80%) was obtained by recrystallization of the crude product from ethanol. Carboxylates **A2–A5** and **B1–B5** were similarly synthesized by refluxing the acid and di-n-butyltin(IV) oxide in 1:1 and 2:1 mole ratio in the mixed solvent with azeotropic removal of water. The related data are listed in Table 1.

Microanalyses (C, H) were determined by the Elemental Analysis Group of Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Tin was estimated as SnO_2. IR spectra were recorded as KBr discs on a Perkin-Elmer 683 Model spectrophotometer in the range 4000–300 cm^{-1}. A JEOL (JNM PMX) 60 MHz spectrometer was used to record the ^1H NMR spectra in CCl_4 with Me_4Si as the internal standard; ^{13}C and ^{119}Sn NMR were recorded in $CHCl_3$ on a Varian FT-80A NMR spectrometer. Chemical shifts were reported in ppm from internal chloroform (77.20 ppm for ^{13}C) and from external 33% Me_4Sn in C_6D_6 for ^{119}Sn.

REFERENCES

[1] S. J. Blunden, A. Chapman: Organotin Compounds in the Environment, in P. J. Craig (ed.): *Organometallic Compounds in the Environment,* Harlow, London (1986).

[2] K. C. Molloy, T. G. Purcell, E. Hahn, H. Schumann, J. J. Zuckerman, *Organometallics, 5,* 1986, 85.

[3] J. Otera, T. Yano, R. Owawara, *Organometallics, 5,* 1986, 1167.

[4] J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, *J. Organomet. Chem., 315,* 1986, 299.

[5] C. Vatsa, V. K. Jain, T. K. Das, E. R. T. Tiekink, *J. Organomet. Chem., 396,* 1990, 9.

[6] K. C. Molloy, S. J. Blunden, R. Hill, *J. Chem. Soc. Dalton Trans.,* 1988, 1259.

[7] W. McFarlane, R. J. Wood, *J. Organomet. Chem., 40,* 1972, C17.

[8] Q. L. Xie, J. Li, Z. Q. Yang, D. K. Zhang, J. T. Wang, *Chinese J. Chem., 9,* 1991, 327.

[9] G. K. Sandhu, N. Sharma, E. R. T. Tiekink, *J. Organomet. Chem., 403,* 1991, 119.

[10] C. S. Parulekar, V. K. Jain, T. Kesavadas, E. R. T. Tiekink, *J. Organomet. Chem., 387,* 1990, 163.

[11] D. C. Gross, *Inorg. Chem., 28,* 1989, 2355.

[12] R. Graziani, G. Bombieri, E. Forsellini, P. Furlan, V. Peruzzo, G. Tagliavini, *J. Organomet. Chem., 125,* 1977, 43.

[13] C. S. Parulekar, V. K. Jain, T. K. Das, A. R. Gupta, B. F. Hoskins, E. R. T. Tiekink, *J. Organomet. Chem., 372,* 1989, 193.

[14] A. Lycka, J. Holecek, *J. Organomet. Chem., 294,* 1985, 179.

[15] G. Domazetis, R. J. Magee, B. D. James, *148,* 1978, 339.

[16] M. Nadvornik, J. Holecek, K. Handlir, A. Lycka, *J. Organomet. Chem., 275,* 1984, 43.

[17] S. W. Ng, C. Wei, V. G. K. Das, *J. Organomet. Chem., 345,* 1988, 59.

[18] R. G. Swisher, J. F. Vollano, V. Chandrasekhar, R. O. Day, R. R. Holmes, *Inorg. Chem., 23,* 1984, 3147.

[19] J. F. Vollano, R. O. Day, D. N. Rau, V. Chandrasekhar, R. R. Holmes, *Inorg. Chem., 23,* 1984, 3153.

[20] R. R. Holmes, R. O. Day, V. Chandrasekhar, J. F. Vollano, J. M. Holmes, *Inorg. Chem., 25,* 1986, 2490.

[21] S. W. Ng, V. G. K. Das, F. van Meurs, J. D. Schaqen, L. H. Shavers, *Acta Crystallogr. C, 45,* 1989, 568.

[22] C. H. Yoder, R. A. Morreall, C. I. Butoi, W. J. Kowalski, J. N. Spencer, *J. Organomet. Chem., 448,* 1993, 59.

[23] H. S. Gutowsky, C. Juan, *J. Chem. Phys., 37,* 1962, 2198.