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^{119m}Sn MÖSSBAUER AND NMR STUDY OF TRIALKYLTIN ACETATES

N. W. G. DEBYE, D. E. FENTON*, S. E. ULRICH AND J. J. ZUCKERMAN**
Department of Chemistry, State University of New York at Albany, Albany, New York 12203 (U.S.A.)

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SUMMARY

Homologous series of trialkyltin acetates in which the methyl group of the acetate is successively chlorinated and fluorinated have been studied by infrared, ^{1}H and ^{19}F NMR and Mössbauer spectroscopies. Substitution by increasingly electron withdrawing groups leads to monotonic increase of the Mössbauer Isomer Shift (*IS*) and NMR $J(^{117,119}\text{Sn–C–}^1\text{H})$ values, and in the methyltin series, of the Mössbauer Quadrupole Splitting (*QS*) values. The data for these five-coordinated, solid-state structures indicate that the effect of halosubstitution is apparently registered predominantly at the carbonyl group whose coordination with tin changes the effective $|\Psi_{5s}(0)|^2$ by shielding. Halosubstitution weakens the donor power of the carbonyl, raising the *IS*; and concentrates *s*-character in the tin–carbon bonds, raising $J(^{117,119}\text{Sn–C–}^1\text{H})$. Likewise, $J(^{117,119}\text{Sn–C–}^1\text{H})$ increases with halosubstitution for the apparently four-coordinated solution species signifying a concentration of *s*-character in the tin–carbon bonds. Five-coordinated, monomeric species may be present in frozen solutions.

INTRODUCTION

Information concerning the structures of organotin compounds can be assembled from a variety of spectroscopic methods in several phases. For example, examination of trimethyltin derivatives in the infrared yields information concerning the configuration of methyl groups about tin, the absence of $\nu_{sym}(\text{SnC}_3)$ being taken as a sign of a planar SnC_3 configuration. In derivatives containing carbonyl groups, the position of $\nu(\text{C=O})$ in the infrared can be used to infer coordination through the carbonyl oxygen and the presence of free carbonyl groups. Infrared data can be obtained from the solid, neat liquid or melt, or solutions. For liquids, or where solubility permits, the NMR $J(^{117,119}\text{Sn–C–}^1\text{H})$ value can be interpreted in terms of the coordination number at tin. The ^{119m}Sn Mössbauer Isomer Shift and Quadrupole Splitting can provide additional information concerning the electron density and site symmetry at the tin nucleus.

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* Present Address: Agricultural Research Council, Unit of Structural Chemistry, Inveresk House, London, W. C. 2, England.

** To whom all inquiries should be addressed.

The organotin acetates are in this view almost ideal model systems for study, and in connection with the recent preparation of a series of trialkyltin acetates in which the methyl group of the acetate is successively chlorinated[1,2] or fluorinated[2,3], we sought to gain further information concerning the nature of these products from ^1H

TABLE 1

^{119m}Sn MÖSSBAUER DATA FOR $R_3SnOC(O)R'$ AT 77°K

R	R'	*IS* (mm/sec)	*QS* (mm/sec)	$\rho = QS/IS$	Γ_1	Γ_2
CH_3	CH_3	1.31±0.02	3.57±0.04	2.72	1.10	1.16
	CH_2F	1.37±0.02	3.86±0.04	2.82	1.04	1.14
	CHF_2	1.40±0.02	4.02±0.04	2.87	1.03	1.04
	CF_3	1.42±0.02	4.18±0.04	2.94	1.14	0.98
n-C_4H_9	CH_3	1.38±0.06	3.71±0.12	2.69	1.33	1.05
		1.45±0.06[a]	3.59±0.12[a]	2.48	0.82	1.15
	CH_2Cl	1.40±0.06	3.94±0.12	2.81	1.12	1.15
	$CHCl_2$	1.47±0.06	4.00±0.12	2.72	1.14	1.14
	CCl_3	1.57±0.06	3.96±0.12	2.52	0.96	1.17
	CH_2F	1.42±0.06	3.96±0.12	2.79	1.24	1.30
	CHF_2	1.59±0.06	3.92±0.12	2.46	1.00	1.16
	CF_3	1.62±0.06	4.04±0.12	2.49	0.96	1.40
		1.54±0.06[a]	3.95±0.12[a]	2.56	0.95	1.10

[a] Frozen solution in cumene.

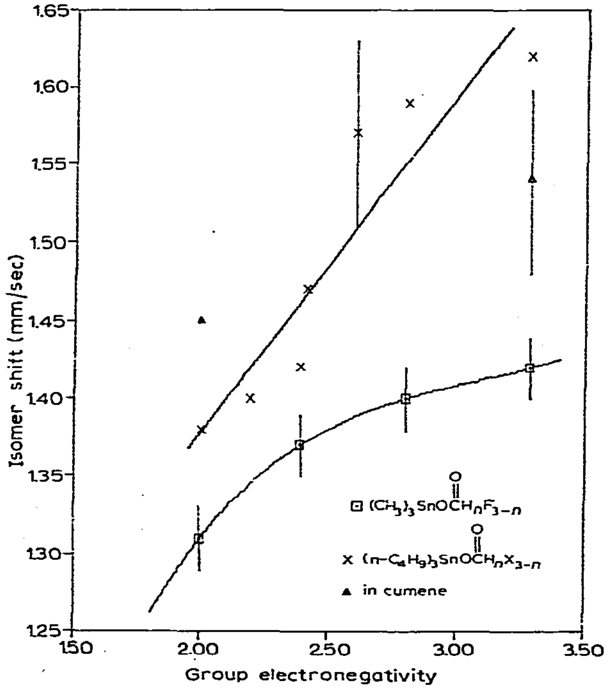

Fig. 1. *IS* of $R_3SnOC(O)CH_nX_{3-n}$ *vs.* the Group electronegativity of CH_nX_{3-n}.

and ^{19}F NMR, infrared and ^{119m}Sn Mössbauer spectroscopies. The recent publication of Poder and Sams[4] includes Mössbauer parameters for seven trimethyltin haloacetates. We report in this paper on eight additional haloacetates and propose a general interpretation of the available data.

EXPERIMENTAL

The compounds studied here have been previously reported. The trimethyltin fluoroacetates were prepared from trimethyltin hydroxide as in Ref. 3. Other samples were supplied by Professors J.-Cl. Maire and C. L. Dillard, and physical properties checked against reported values.

Infrared spectra were recorded on Beckman IR-8 and IR-10 instruments. NMR measurements were made on Varian Associates HR-60 and HA-100 spectrometers using a tetramethylsilane standard for the butyltin compounds, a chloroform standard for the methyltin compounds in the proton work, and a fluorotrichloromethane standard in the fluorine-19 work. Proton parameters were measured using a Hewlett Packard Model 521C electronic counter to measure the difference between the frequencies produced by the sweep and lock oscillators of the Varian HA-100 spectrometer. Fluorine-19 parameters were determined by standard sidebanding techniques using a Hewlett Packard Model 200AB audio oscillator and Model 521C electronic counter. ^{119m}Sn Mössbauer spectra were recorded on our cam-drive, constant acceleration spectrometer previously described[5] using a $BaSnO_3$ source (New England Nuclear Corp.). In light of the report that the *IS* values of the trimethyltin haloacetates can be considered as constant[4], we undertook to test the small, but reproducible differences we initially found in our compounds. In one series of experiments the spectrum of β-tin (N.B.S.) at room temperature, which we take as 2.56 mm/sec, was recorded before and after each run. In a second series of experiments each compound was mixed as a fine powder with tetraphenyltin which served as an internal standard. In each case the relative shifts were studied several times and found to be reproducible. The data have not been averaged. Our curve fitting program is developed from a treatment of the least squares solution of non-linear equations (Taylor Series expansion about estimated parameters) similar to that of Wentworth[6], and assumes that the curves are Lorentzian doublets without further constraints. Adding the constraint of equal linewidths does not significantly change the *IS* or *QS* values.

RESULTS

Table 1 lists the ^{119m}Sn Mössbauer data taken at 77°K for the homologous series of trialkyltin haloacetates. The spectra show well-resolved doublets in each case. The *IS* values are listed with respect to SnO_2 (room temperature), using β-tin as the standard. The *IS* increases with successive halosubstitution as shown in Fig. 1 where these values are plotted against the group electronegativity[7] of the halomethyl group of the acetate. The *QS* values in the methyltin series likewise increase generally with halosubstitution as shown in Fig. 2, and this trend holds for frozen solutions in cumene as well. The tributyltin series, however, exhibits a pronounced saturation effect in the variation of *QS* with group electronegativity. Both the *IS* and *QS* data were plotted as well against the Taft inductive factor σ^{*8} as in Ref. 4. The use of σ^* instead of the

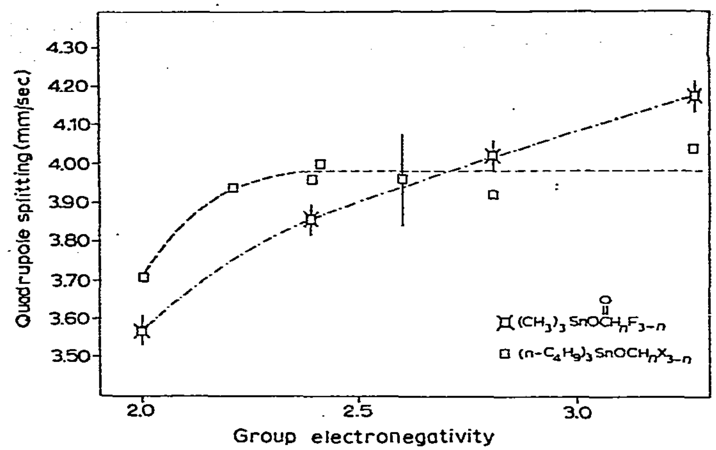

Fig. 2. *QS* of $R_3SnOC(O)CH_nX_{3-n}$ *vs.* the Group electronegativity of CH_nX_{3-n}.

TABLE 2

^{1}H AND ^{19}F NMR DATA AT 100 AND 56 MHz RESPECTIVELY FOR $R_3SnOC(O)R$

R	R'	$\delta(C(O)C\text{-}H)^{a,b}$	$\delta(F)^c$	$\delta(Sn\text{-}C\text{-}H)^{a,b}$	$J(^1H\text{-}C\text{-}^{19}F)^d$	$J(^{117,119}Sn\text{-}C\text{-}^1H)^d$		$(J^{119}/J^{117})^e$
CH_3	CH_3	201.0		51.5		55.9	58.4	1.046
	CH_2F	476.6	12518±5	60.6	47.8	55.9	58.5	1.046
	CHF_2	581.5	7062±5	63.9	54.4	56.0	58.6	1.046
	CF_3		4293±2	68.4		57.4	60.0	1.045
n-C_4H_9	CH_3	191.4						
	CH_2F	462.0	12404±5		48.7±0.2			
	CHF_2	569.7	7014±4		55.0			
	CF_3		4249±2					

[a] Relative to a tetramethylsilane lock signal for the butyltin compounds. A conversion factor of 724.3 Hz was used to adjust the data for the methyltin compounds from the chloroform lock signal to tetramethylsilane. [b] Experimental error ±0.2 Hz. [c] Relative to $CFCl_3$. [d] Experimental error ±0.1 Hz. [e] Theoretical value for this ratio is 1.046.

group electronegativity values places the *QS* data for the methyltin acetates on a straight line in agreement with the authors of Ref. 4, but offers no advantages in the treatment of the butyltin data. The compounds were examined as fine, polycrystalline powders and each of the spectra recorded here showed some asymmetry of the component lines of the doublet.

Table 2 lists the ^{1}H NMR data taken at 100 MHz and the ^{19}F NMR data taken at 56 MHz. The general increase in proton chemical shifts and decrease in fluorine chemical shifts with increasing substitution by fluorine on the acetate group are those expected on the basis of simple electron withdrawal, and this effect has been seen in the analogous chloroacetates[3]. The methyltin protons are similarly affected by halosubstitution of the acetate, but in a much less drastic way.

The two-bond $J(^{117,119}Sn\text{-}C\text{-}^1H)$ in the methyltin acetates in chloroform solution (5% by wt.) increases generally with the group electronegativity of the CH_nX_{3-n} group, and these data are plotted in Fig. 3 along with data previously reported for chloroform solutions (3–5% by wt.)[3]. ^{117}Sn and ^{119}Sn data are separate

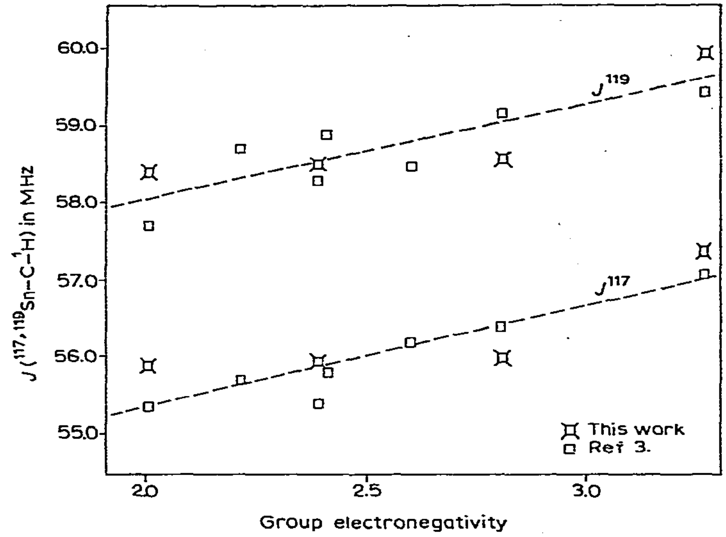

Fig. 3. $J(^{117,119}\mathrm{Sn{-}C{-}^1H})$ of $(CH_3)_3SnOC(O)CH_nX_{3-n}$ *vs.* the Group electronegativity of CH_nX_{3-n}.

measurements and are plotted separately. The points were fit to a straight line with a weighted least squares program. It was found that virtually the same fit resulted from using the data from ref. 3, our own data, or all. The equations of the lines were found to be $J^{117}=1.32X_i+52.73$ and $J^{119}=1.21X_i+55.65$. The ratio of the intercepts at $X_i=0$ should be the theoretical J^{119}/J^{117} ratio (1.046); we find 1.055.

DISCUSSION

In general the *IS* for organotin(IV) compounds is thought to measure changes in the density of *s*-electrons at the nucleus, mainly $|\Psi_{5s}(0)|^2$ for tin[9]. In a simple view the progressive substitution of increasingly electron withdrawing groups should lower this value by an inductive effect. Table 1, however, shows a small, but monotonic increase of *IS* with successive replacement by halogen atoms. Thus, increasing the group electronegativity of the methyl group of the acetate apparently raises the *s*-electron density at tin (see Fig. 1).

The structure and bonding of the triorganotin carboxylates have been extensively investigated and discussed[10]. It is generally agreed that the tin atom is usually five-coordinated in the solid through bridging carboxylate groups, and X-ray crystallographic data is now available[11,12] to confirm this suggestion originally put forward on the basis of infrared work[13,*,**].

The methyltin compounds seem somewhat anomalous since substitution of

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[*] The failure to observe a Mössbauer resonance for the alkyltin carboxylates at ambient temperatures[23,24] cannot be taken as contradictory since it appears that the precise relationship between the Mössbauer recoil-free fraction and coordination number or microstructure is very complex.[25]

[**] Apparently the bulky neophyl group serves to convert its monoacetate derivative to a monomer in the solid trineophyltin acetate[26], and a recent crystallographic study of tricyclohexyltin acetate confirms the monomeric nature of this compound[27].

larger organic groups on tin gives rise to a decrease in the reported identity period; whereas in other alkyltin carboxylates substitution of larger alkyl groups increases the repeat distance as does successive chloro-substitution. In the infrared of the solid alkyltin acetates the bands assigned to $\nu_{\text{asym}}(\text{COO})$ increase generally, and those assigned to $\nu_{\text{sym}}(\text{COO})$ decrease generally with successive substitution by chlorine[1,2,14] or fluorine[2].

We offer the following interpretation of these data: The population of the empty 5*d*-orbitals of the tin atom by electron pairs from the carboxyl oxygen atom would be expected to lower the effective $|\Psi_{5s}(0)|^2$ by shielding, and thus lower the *IS* relative to the value found in a monomer with an organic ester structure. The subsequent weakening of the Lewis base strength of the carbonyl by the inductive pull of the halomethyl group in the $X_nH_{3-n}C(O)O-$ system could account for the observed incremental increase in *IS*. A second-order contribution might result from the improved acceptor power of tin on halosubstitution*. While it is difficult to separate the observed increase in identity period for the successively chloro-substituted tri-n-butyltin acetates precisely into the factors responsible, the distance is observed to change in the direction expected for an incremental weakening of the intermolecular association. The effect of the inductive pull is also seen in the changes in ν_{asym} and $\nu_{\text{sym}}(\text{COO})$: an increase in inductive pull from the carbon atom α- to the carbonyl should give rise to an increase in frequency, while increasing mass at that position will decrease it. Apparently the mass effect predominates in determining changes in $\nu_{\text{sym}}(\text{COO})$ of the chloroacetates[1,2,14] while the inductive effect is more important in the ν_{asym} of both the fluoro-[2] and chloro-acetates[1,2,14]. In the fluoro-substituted derivatives the relative importance of the inductive effect would be increased, and this is seen in the observed increase of ν_{sym} with successive fluoro-substitution[2]. These changes support the view that the inductive effect of halo-substitution is registered predominately at the carbonyl group. In the ω-chlorodibutyltin carboxylates the effect of the substitution on the Mössbauer parameters is seen to drop off to within experimental error for the longer chain organic acids[15].

On the basis of isovalent hybridization arguments[16], the *s*-character of the hybrid orbitals directed from the tin atom will tend to be concentrated in the bonds to carbon, leaving the tin–oxygen bond relatively more *p*. Coordination by carbonyl oxygen apparently further skews the imbalance of this distribution. NMR $J(^{119}\text{Sn}-\text{C}-^{1}\text{H})$ for methyltin compounds of coordination numbers four to six show a steady

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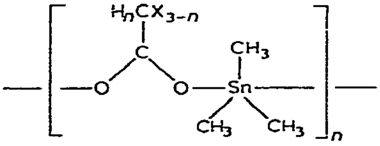
* The effect of changing the mass of the rigid system



on the magnitude of the Isomer Shift can be evaluated through the expression for the second-order Doppler Shift[28,29]:

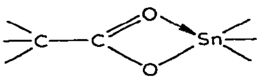
$$[IS]_{\text{Doppler}} = \frac{E_{\text{kinetic}}}{m\cdot c^2}\cdot E_\gamma$$

where an increase in mass along our series $CH_3 < CH_2F < CH_2Cl \approx CHF_2 < CF_3 < CHCl_2 < CCl_3$, would *decrease* the IS, contrary to our observations.

increase, presumably arising through an increased concentration of *s*-character in the tin-carbon bond on coordination[30]. Any removal of electron density by an inductive pull through the $\geqslant$C–C(O)O–Sn system would tend to intensify this concentration of *s*-character in the tin–carbon bonds and lead to the general increase in both the $J(^{119}\text{Sn–C–}^{1}\text{H})$* and *QS* values with halogen substitution as seen in Fig. 1 and 2. The magnitudes of the observed *QS* values are all such as to give $\rho(=QS/IS) \geqslant 2.1$, reflecting pentacoordination[17].

The *IS* of the tri-n-butyltin acetate and trifluoroacetate measured in frozen dilute solution in cumene are very close. Infrared studies at room temperature on these samples show $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ at frequencies characteristic of the monomeric compound, with free, "normal-ester" carbonyl groups (1635 and 1303 cm^{-1} for the acetate, and 1720 and 1400 cm^{-1} for the trifluoroacetate, respectively) as has also been observed in carbon tetrachloride solution[2,18], and for the trimethyltin acetate and chloroacetate in chloroform solution[19].

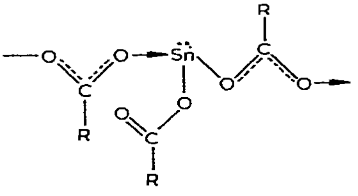
At the liquid nitrogen temperatures at which the Mössbauer spectra of these frozen solutions were recorded, however, it is possible that structures such as (I)



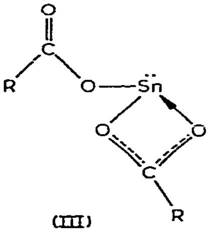
(I)

might be stabilized**.

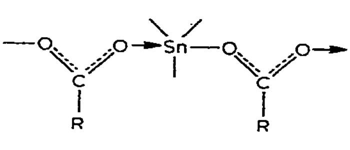
In the analogous tin(II) carboxylates both the *IS* and *QS* values decrease generally with halogen substitution[20], and the suggestion of three-coordination for the tin atom has received support from far-infrared studies[21]. The pyramidal three-coordinated tin(II) configuration involving either inter- (II) or intra-molecular (III) carboxylate bridging bonds differs from the structure of the trialkyltin(IV) carboxylates (IV) in that there is always one normally bound carboxylate ester group in the former:



(II)



(III)



(IV)

Halomethyl substitution in an acetate group bound as in an organic ester can result only in the simple removal of electron density from tin with the concomittant lowering

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* The authors of ref. 4 chose to ignore these differences in the NMR *J* value data (not listed) for their compounds.

** Such *intra*molecular chelation has been postulated for the dialkyltin diacetates in solution[31].

of the *IS*. This observed decrease[20] argues against a structure with four-coordination at tin(II) which might allow all the carboxylate groups involved to coordinate either by bridging or by chelation. The amount of *s*-character in these tin–oxygen bonds probably approaches zero since *s*-character is concentrated in the lone pair electrons in this valence state. Thus the arguments used to rationalize the changes in *QS* for the trialkyltin(IV) carboxylates are inapplicable here.

In a recent study of $\geqslant\mathrm{Sn{-}CH_2{-}X}$ systems where X=F, Cl and various oxygen- and nitrogen-containing ligands it was seen that the *IS* value for these presumably monomeric compounds was insensitive to the substitution of methyl hydrogen by various electron-withdrawing groups[22]. Thus the methylene group in $\mathrm{R_3SnCH_2X}$ serves to insulate the tin atom from the effect of changes in X. Changes in X in compounds of the type $\mathrm{R_3SnX}$, on the other hand, produce large differences in Mössbauer parameters. Thus our compounds, $\mathrm{R_3SnOC(O)CH_nX_{3-n}}$, can be said to lie in an intermediate position with respect to the transmission of effects.

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