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Mössbauer Effect of ^{119}Sn in Some Organotin Compounds[*1]

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Mössbauer, NMR, and infrared spectroscopy have been applied to the study of a number of organometallic tin compounds containing one or more tin manganese pentacarbonyl bonds. For the $(CH_3)_{4-n}Sn[Mn(CO)_5]_n$ series ($n=0$ to 3) a linear relation between the Mössbauer isomer shift and the number of manganese pentacarbonyl ligand was consistent with the partial isomer shift theory of ^{119}Sn. A linear relation between the Mössbauer isomer shift and the methyl proton NMR chemical shift was also observed for this series. A plot of the isomer shift (δ_0) *versus* the number of p holes (h_p) for organotin manganese pentacarbonyl compounds established a relation $\delta_0=1.23+0.53\,h_p$ for sp^3 hybridized tin. From isomer shift systematics a value of $(\Delta R/R)$ for ^{119}Sn was calculated to be 1.2×10^{-4}.

The preparation and properties of some mixed metal carbonyl compounds of the type $R_{4-n}Sn[Mn(CO)_5]_n$ were R=Cl, Br, C_6H_5, CH_3 and $n=0$ to 3 have been reported by Gorsich.[1] Clark and Tsai,[2] and Jetz and his co-workers[3] have studies the tin manganese bond by IR and NMR spectroscopy. Later, Graham,[4] using the Cotton-Kraihanzel (CK) approximate force constant method, separated the inductive and mesomeric effects in these types of compounds. The Mössbauer effect of a variety of these tin-transition metal bonds in organometallic compounds have been studied by Karasev[5] and his group to obtain information on the nature of the Sn–Mn(CO)$_5$ interaction, the tin-alkyl sites and the local symmetry of Mn(CO)$_5$ group in the compounds. Values of electron density at the nucleus were obtained from Ruby *et al.*[6] correlation diagram of electron density at the nucleus and the isomer shift. From this a value of $(\Delta R/R)$ is obtained.

TABLE 1. MÖSSBAUER PARAMETERS OF PREPARED AND RELATED TIN COMPOUNDS AT 80°K

Compounds	Isomer shift* δ_0 (mm/sec)	Quadrupole splitting ΔE (mm/sec)
$Cl_3Sn[Mn(Co)_5]$	1.63	1.62
$Br_3Sn[Mn(Co)_5]$	1.74	1.77
$\phi_3Sn[Mn(CO)_5]$	1.51	0.00
$(CH_3)_4Sn$**	1.30	0.00
$(CH_3)_3Sn[Mn(CO)_5]$	1.46	0.81
$(CH_3)_2Sn[Mn(Co)_5]_2$	1.68	0.92
$(CH_3)Sn[Mn(Co)_5]_3$	1.83	0.95

* Isomer shift relative to $BaSnO_3$ absorber

** Parameters previously reported by several works

Experimental

The compounds reported in Table 1 save the monomethyl tin tris manganese pentacarbonyl, were synthesized by Gorsich's procedure.[1] A new method utilizing an inert N_2 atmosphere because of the air sensitivity of the manganese pentacarbonyl dimer was used to prepare the monomethyl tin tris manganese pentacarbonyl. An approximately 1% Na amalgam (0.5 g Na and 50 g Hg) was reacted with 2 g (5.1 mmol) $Mn_2(CO)_{10}$ dissolved in 30 m*l* of dried tetrahydrofuran. The reaction mixture was stirred for 1 hr with a magnetic stirrer and the resulting $Na^+[Mn(CO)_5]^-$ solution was decanted off from the Hg. The latter solution was mixed with 0.82 g (3.4 mmol) $MeSnCl_3$ dissolved in 4 m*l* of THF and stirred for three hours. The solid residue was filtered off and the THF solvent was removed from the mother liquor with a water aspirator. The solid residue was extracted with a 1 : 2 by volume water - THF mixture and the crude product was recovered by removing the THF from the organic layer. This yellow solid was recrystallized from *n*-hexane.

All the compounds studied gave satisfactory analytical data.

The Mössbauer spectra of these compounds at 80°K were obtained in transmission geometry with a Ba-$^{119m}SnO_3$ source at room temperature. In addition proton magnetic resonance and IR spectroscopic data were taken.

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1) R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2486 (1962).

2) H. C. Clark and J. H. Tsai, *Inorg. Chem.*, **5**, 1407 (1966).

3) W. Jetz *et al.*, *Inorg. Chem.*, **5**, 2217 (1966).

4) W. A. Graham, *ibid.*, **7**, 315 (1968).

5) A. Karasev *et al.*, *Teor. Eksp. Khim.*, **2**, 126 (1966).

6) S. L. Ruby *et al.*, *Phys. Rev.*, **159**, 239 (1967).

Table 2. Mössbauer and proton magnetic resonance parameters of $(CH_3)_{4-n}Sn[Mn(CO)_5]_n$ ($n=0$ to 3) compounds

Compound	Isomer shift δ_0 (mm/sec)	Quardrupole splitting ΔE (mm/sec)	Proton chemical shift (ppm)	$J(^{119}Sn-CH_3)$ cps
Me_4Sn	1.23	0.00	9.93	54.0
$Me_3Sn[Mn(CO)_5]$	1.46	0.81	9.54	48.3
$Me_2Sn[Mn(CO)_5]_2$	1.68	0.92	9.14	36.7
$MeSn[Mn(CO)_5]_3$	1.83	0.95	8.67	—

Results and Discussion

In Table 1 the Mössbauer parameters of the ^{119}Sn compounds prepared in this laboratory are reported. The quadrupole splitting in these compounds save triphenyl tin manganese pentacarbonyl are due to p holes in the "perfect" s state of sp^3 configuration arising from a disparity between the electronegativity of the R (Cl, Br, CH_3) group and the manganese pentacarbonyl radical. The question of why there is no observed quadrupole splitting in triphenyl tin manganese pentacarbonyl although there is a "p" electron defect ($h_p=0.57$) which is larger than in the trimethyl tin manganese pentacarbonyl ($h_p=0.42$) where there is a measurable quadrupole splitting is still not resolved. A reasonable guess is that the presence of the π electron clouds in the phenyl rings compensates for the field inhomogeneity at the tin nucleus and hence there is no resolvable quadrupole interaction.

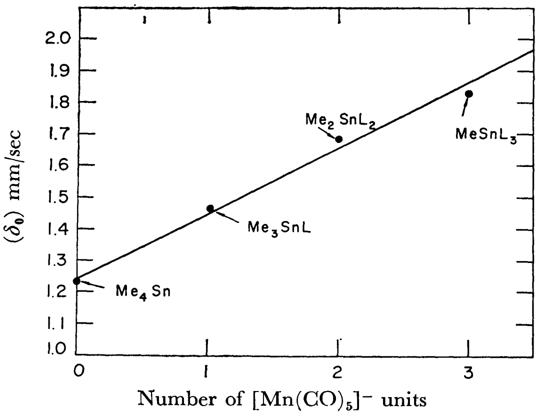

Fig. 1. A plot of the isomer shift *versus* the number of substituted $[Mn(CO)_5]$ ligand for the $(CH_3)_{4-n}Sn[Mn(CO)_5]_n$ series. ($n=0$ to 3)

Particularly interesting is the $(CH_3)_{4-n}Sn[Mn(CO)_5]_n$ series where $n=0$ to 3. The electrical environment around the metal atom in tetramethyl tin gives rise to the expected zero quadrupole splitting, whereas the trimethyl, the dimethyl and the monomethyl tin congeners show an almost constant quadrupole splitting of approximately

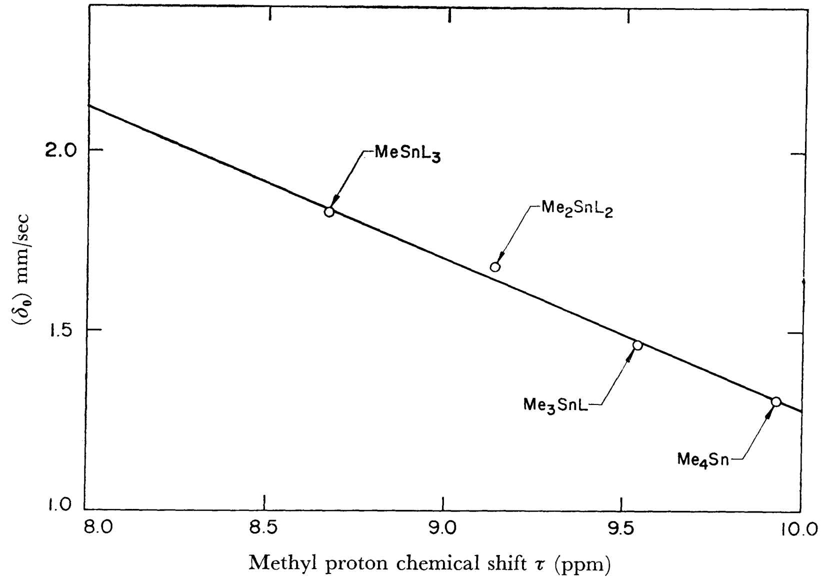

Fig. 2. Graph of the Mössbauer isomer shift *versus* the methyl proton NMR shift for the $(CH_3)_{4-n}Sn[Mn(CO)_5]_n$.

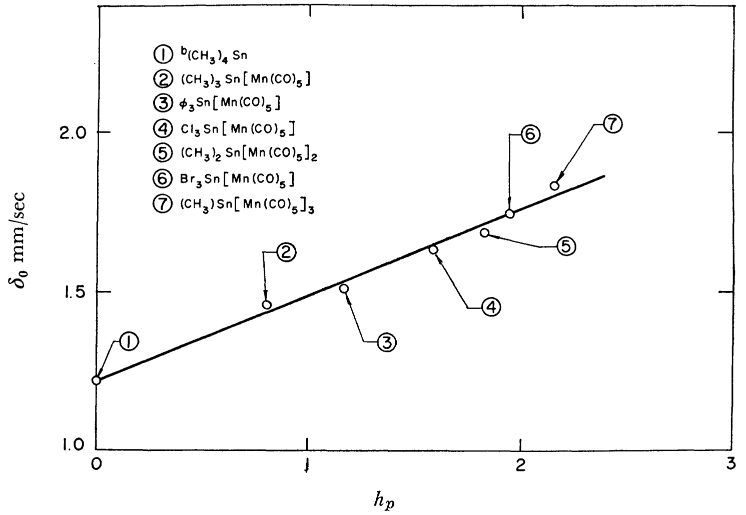

Fig. 3. A plot of the ismer shift δ_0 *versus* the number of p holes h_p for tin manganese pentacarbonyl compounds.

1 mm/sec. This lack of variance is explained by the disparity yet closeness of the group electronegativety of the $[Mn(CO)_5]$ ligand of 2.01 compared to the methyl group of 2.54.

Figure 1 shows a linear plot of the isomer shift δ_0 *versus* the number of $[Mn(CO)_5]$ ligands in the series $(CH_3)_{4-n}Sn[Mn(CO)_5]_n$, where $n=0$ to 3. This in fact lends proof to the partial isomer shift theory of tin and leads to the simple equation.

$$\delta_0(\text{relative to BaSnO}_3) = 1.23 + 0.19n \qquad (1)$$

Another interesting feature of this series is seen in Fig. 2. It establishes a linear relation between the Mössbauer isomer shift (δ_0) and the proton NMR shift τ (ppm). Holmes and Kaesz[7] have correlated the coupling constant $A_{^{119}\mathrm{Sn}\mathrm{H}}$ with %5s character. This correlation does not work for this series and may be due to hydrogen bonding of the methyl protons in juxtaposition with oxygen of the manganese pentacarbonyl moiety. Evidence for change in local C_{4v} symmetry of the bulky manganese pentacarbonyl ligand in the monomethyl tin tris manganese pentacarbonyl derivative was furnished by the drastic change in the relative intensity of the $[2A_1+E]$ bands. It is possible that smaller changes of this sort in the other member of this series may not be detected by infrared techniques.

Spijkerman[8] has calibrated the %5s character and the Mössbauer chemical shift. From the measured isomer shift, %5s character of all compounds in this work was estimated, and electronic configurations and number of p holes h_p assuming a constant sp^3 hybridization calculated. These are shown in Table 3. Figure 3 shows a plot of the isomer shift δ_0 *versus* the number of p holes h_p leads to a linear relationship $\delta_0=1.23+0.53\ h_p$ for sp^3 hybridized tin.

TABLE 3. DERIVED PARAMETERS FROM THE ISOMER SHIFTS OF ^{119}Sn COMPOUNDS

Compounds	Electronic configuration	Number of p holes h_p	% 5s character
$Cl_3Sn[Mn(CO)_5]$	$5s^{0.74}5p^{2.22}$	0.78	34
$Br_3Sn[Mn(CO)_5]$	$5s^{0.68}5p^{2.04}$	0.96	37
$\phi_3Sn[Mn(CO)_5]$	$5s^{0.81}5p^{2.43}$	0.57	31
$(CH_3)_4Sn$	$5s^1\quad 5p^3$	0.00	25
$(CH_3)_3Sn[Mn(CO)_5]$	$5s^{0.86}5p^{2.58}$	0.42	29
$(CH_3)_2Sn[Mn(CO)_5]_2$	$5s^{0.70}5p^{2.10}$	0.90	36
$(CH_3)Sn[Mn(CO)_5]_3$	$5s^{0.64}5p^{1.92}$	1.08	39

Ruby *et al.*[6] has correlated the electron density $\psi^2\ (0)/a_0^3$ at the nucleus and the isomer shift for ^{119}Sn. From this data values of $\psi^2(0)/a_0^3$ were obtained and a value of $\Delta R/R=1.2\times10^{-4}$ calculated. This agrees with the value obtained by their group and some previously reported values.

Further work is in progress to clear up any ambiguities in the phenyl tin manganese pentacarbonyl series.

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[7] R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

[8] J. Spijkerman, "Advances in Chemistry Series," No. 68, "The Mössbauer Effect and Its Application in Chemistry," 1967, p. 105.