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The Mössbauer Effect in Ethyltin Halides and Related Compounds

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The Mössbauer spectra for ethyltin halides and related compounds (Et_4Sn, SnX_4 (X=Cl,Br, I), Et_3SnX, Et_2SnX_2 (X=Cl, Br, I), $EtSnI_3$) were obtained. The replacement of ethyl groups by halogen atoms made the isomer shifts more positive relative to the tetraethyltin precursor. These results may be explained in terms of the rehybridization theory that the *s*-character of a central atom tends to concentrate in orbitals directed toward electropositive substituents. A suggestion that the compounds of $RSnX_3$ type show smaller quadrupole splittings than the R_3SnX compounds is made and discussed in terms of the rehybridization in the orbitals of the tin atom and in terms of bond ionicity.

The ^{119}Sn-Mössbauer parameters in organotin compounds provide some useful information about the nature of the chemical bond formed by the tin atom. Among them, the isomer shift depends on the *s*-electron density at the tin nucleus. Changes in the electron density at the tin nucleus arise primarily through changes in the valence 5*s*-electrons, but other valence 5*p*- and 5*d*-electrons can shield 5*s*-electrons from the tin nucleus.[1a] An increase in the isomer shift corresponds to an increase in the *s*-electron density at the tin nucleus.[1b] Alkyl- and aryltin halides show positive isomer shifts compared to the corresponding tetraalkyl- and tetraaryltin.[1a,2–5] These findings on isomer shifts cannot be interpreted only in terms of polarization due to the electronegativity of the bonding halogen atoms. Stöckler and Sano have made a plausible suggestion that the tin *d*-orbital electron donated to the halogen atom may antishield the tin nucleus from the *s*-electron.[4] In the present study, similar results for ethyltin halides were obtained. Further, diethyltin dihalides showed an obvious dependence of the isomer shift on the halogen atoms. These results may be interpreted in terms of both the rehybridization of tin valence orbitals and the polarization due to the bonding halogen atoms. Very large quadrupole splittings were observed for triethyltin halides and diethyltin dihalides, whereas for ethyltin triiodide the splitting was drastically reduced. The fact that the compounds of $RSnX_3$ type (X=halogen or pseudohalogen, R=alkyl or aryl group) show smaller quadrupole splittings than the R_3SnX compounds will be discussed in terms of the rehybridization in the valence orbitals of the tin atom and in terms of bond ionicity.

Experimental

The compounds used in the present study were prepared by published procedures.[6,7] All of the triethyltin halides and ethyltin triiodide were purified by fractional distillation at a reduced pressure. The diethyltin dihalides were washed with ether and dried at a reduced pressure. The elemental analyses of C and H gave almost completely satisfactory results. The ^{119m}Sn-Mössbauer spectra were taken using a constant acceleration electromagnetic driver previously reported on.[8] The source was Pd^{119m}Sn, containing about 0.2 mCi^{119m}Sn. The source was operated at room temperature, while the absorbers were cooled with liquid nitrogen in a cryostat previously reported on.[8] The velocity scale has been calibrated by the isomer shifts of β-Sn and SnO_2. The isomer shifts of β-Sn and SnO_2 are +1.11 and −1.58 mm/sec respectively with respect to Pd^{119m}Sn.

Results and Discussion

The Mössbauer parameters for ethyltin halides and related compounds are presented in Table 1. The Mössbauer spectra of Et_4Sn, Et_3SnCl, and Et_2SnCl_2 are shown in Fig. 1. The dependences of the isomer shifts on halogen atoms bonding to tin and on their number are shown in Fig. 2. Parish and Platt reported the quadrupole splittings of Et_nSnX_{4-n} (n=1, 2, 3, X=Cl, Br, I), with the exception of $EtSnI_3$ but their results do not agree with ours.[9] On the other hand, Bryuchova *et al.* presented quadrupole splittings and

TABLE 1. MÖSSBAUER PARAMETERS FOR TIN HALIDES

Compounds[a]	I.S.(*vs*.Pd^{119m}Sn)[b]	Q.S.[b]
Et_4Sn	−0.15 mm/sec	0 mm/sec
$SnCl_4$	−0.70[c]	0
Et_3SnCl	+0.11	3.84
Et_2SnCl_2	+0.20	3.78
$SnBr_4$	−0.40	0
Et_3SnBr	+0.14	3.42
Et_2SnBr_2	+0.23	3.48
SnI_4	+0.05	0
Et_3SnI	+0.09	3.09
Et_2SnI_2	+0.32	3.24
$EtSnI_3$	+0.18	1.77

a) Et=C_2H_5, b) ±0.03 mm/sec c) Ref. 19.

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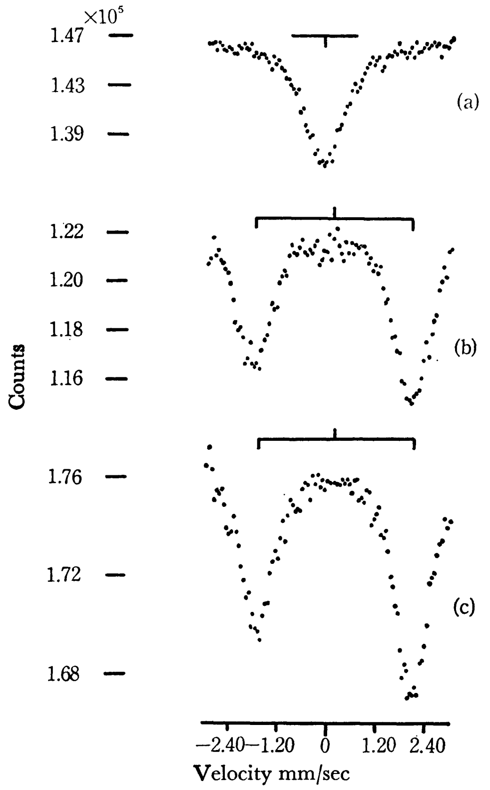

Fig. 1. Mössbauer spectra of Et_4Sn (a), Et_3SnCl (b) and Et_2SnCl_2 (c).

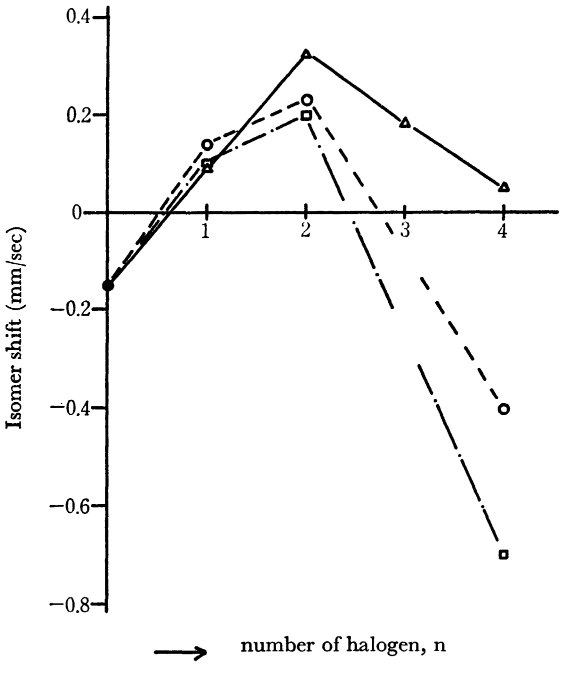

Fig. 2. Dependences of the isomer shifts on number of halogen substituents in ethyltin halides, $Et_{4-n}SnX_n$.
X=I; △, Br; ○, Cl; □, Et_4Sn; ●

isomer shifts consistent with our results for Et_3SnBr and Et_2SnI_2; that is, they reported that Et_3SnBr and Et_2SnI_2 showed the quadrupole splittings of 3.45 and 3.21 mm/sec and isomer shifts of −0.48 and −0.33 mm/sec relative to α–Sn, which could be converted to shifts of +0.12 and +0.27 mm/sec respectively relative to PdSn.10)

Isomer Shift. Ethyltin halides showed more positive isomer shifts than did tetraethyltin. The isomer shifts in dihalides were more positive than those in monohalides. These results indicate that the *s*-electron density at the tin nucleus increase with an increase in the isomer shifts; $Et_4Sn<Et_3SnX<Et_2SnX_2$. Similar results for alkyl- and aryltin halides have been reported.2–5) It may seem that the electron-withdrawing abilities of halogen atoms should decrease the 5*s*-electron density at the tin nucleus. Moreover, the 5*p*-electrons, which can shield 5*s*-electrons from the tin nucleus, may be decreased in the same way, but the decrease in the 5*p*-electron cannot compensate for the decrease in the 5*s*-electron density at the tin nucleus.11) Hence, these results on isomer shifts cannot be interpreted only in terms of polarization due to the electronegativity of the halogen atoms. Stöckler and Sano have interpreted these results in terms of the deshielding by the tin *d*-orbital participated in $d\pi$–$p\pi$ bonding with halogen atoms.4) However, the way in which the *d*-electron deshields the *s*-electron from the tin nucleus is ambiguous. Devooght *et al.* suggested that all the halides, with the exception of trimethyltin halides, could be tetracoordinated monomers.12) The far-infrared spectra obtained in this study for ethyltin halides with neat samples sandwiched between CsI plates or nujol mulls showed the same Sn–C stretching frequencies as that in a previously-reported cyclohexane solution, in which ethyltin halides were tetrahedral monomers.13) Bent proposed the following theory on the basis of the effects of the orbital hybridization and the electronegative substituents on the bond angles, bond lengths, and other physical properties.14) He mentioned that the *s*-character of a central atom tends to be concentrated in orbitals directed toward electropositive substituents. This rule can explain our findings on the isomer shifts. That is, the *s*-character in tin valence orbitals is concentrated in the orbitals toward the more electropositive ethyl groups (in general, alkyl groups), while the *p*-character is concentrated in the orbitals directed to the electronegative halogen atoms. Moreover, the bonds directed to halogen atoms are more ionic due to their electronegativity. The increased ionicity in an orbital with a predominant *p*-character leads to an increase in the *s*-electron density at the tin nucleus due to decreased shielding by the *p*-electron. For triethyltin halides, the dependence of the isomer shifts on the bonding halogen atoms is not evident. However, it is obvious for diethyltin dihalides, in the case of which it coincides with the order of halogen electronegativity. Therefore, it may be assumed that the rehybridization effect is predominant

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for triethyltin halides, while, for diethyltin dihalides, the polarization effect due to the electronegativity of halogen atoms is comparable to the rehybridization effect.

Quadrupole Splitting. The quadrupole splittings for mono- and dihalides increased in the order; iodides<bromides<chlorides. These results are consistent with the observations previously published.[2-5,9,10] The splitting of ethyltin triiodide was drastically reduced. Similar results for trihalides have been reported in several pairs of compounds. Stöckler and Sano reported that the splittings for $(C_6H_5)_3SnCl$ and $C_6H_5SnCl_3$ were 2.46 and 1.80 mm/sec respectively, while for $(CH_3)_3SnBr$ and CH_3SnBr_3 they were 3.28 and 1.91 mm/sec respectively.[4] Moreover, Gassenheimer and Herber reported similar results for alkyltin pseudohalides[15] (for $(C_4H_9)_3SnSCN$ and $C_4H_9Sn(SCN)_3$, 3.88 and 1.46 mm/sec, respectively). Consequently, it seems to be a general rule that the compounds of the $RSnX_3$ type (X=halogen or pseudohalogen, R=alkyl or aryl group) show smaller quadrupole splittings than the compounds of the R_3SnX type in cases where these compounds are monomeric. This can be understood if we consider the field gradient at the tin nucleus in the following model. From the fact previously mentioned, we assume a C_{3v} symmetry around the tin atom for $RSnX_3$. The four valence hybrid orbitals of the tin atom are as follows;

$$\begin{aligned}
\varphi_1 &= C_R\varphi_s + (1-C_R{}^2)^{1/2}\varphi_{p(z)} \\
\varphi_2 &= C_X\varphi_s + (1-C_X{}^2)^{1/2}(\varphi_{p(z)}\cos\alpha - \varphi_{p(x)}\sin\alpha) \\
\varphi_3 &= C_X\varphi_s + (1-C_X{}^2)^{1/2}(\varphi_{p(z)}\cos\alpha + \frac{1}{2}\varphi_{p(x)}\sin\alpha \\
&\qquad - \frac{\sqrt{3}}{2}\varphi_{p(y)}\sin\alpha) \\
\varphi_4 &= C_X\varphi_s + (1-C_X{}^2)^{1/2}(\varphi_{p(z)}\cos\alpha + \frac{1}{2}\varphi_{p(x)}\sin\alpha \\
&\qquad + \frac{\sqrt{3}}{2}\varphi_{p(y)}\sin\alpha)
\end{aligned} \tag{1}$$

where α is the angle between the direction of the tin-carbon bond (z axis) and that of the tin-halogen bonds, where φ_s and φ_p are the tin valence $5s$ and $5p$ orbitals, and where C_X and C_R are the s-character of the hybrid orbitals directed to alkyl group and to the halogen atoms respectively. From the orthogonality of φ_1 with φ_2, we obtain;

$$\cos^2\alpha = \frac{C_R{}^2 C_X{}^2}{(1-C_R{}^2)(1-C_X{}^2)} \tag{2}$$

and from the orthogonality of φ_3 with φ_4, we obtain;

$$C_X{}^2 = \frac{1-3\cos^2\alpha}{3\sin^2\alpha} \tag{3}$$

The four molecular orbitals are;

$$\begin{aligned}
\psi_1 &= \frac{\varphi_1 + i_R\varphi_R}{(1+i_R{}^2)^{1/2}} \\
\psi_j &= \frac{\varphi_j + i_X\varphi_X}{(1+i_X{}^2)^{1/2}}, \quad j = 2, 3, 4
\end{aligned} \tag{4}$$

where φ_R and φ_X are the valence atomic orbitals of carbon and halogen, and where i_R and i_X are their characters in the appropriate molecular orbitals.

The field gradient, $(V_{zz})_j$, due to electrons in the molecular orbital, ψ_j, is given by the expectation value of the field gradient operator, H_q $(H_q = \frac{3\cos^2\theta - 1}{r^3})$;

$$(V_{zz})_j = 2\langle\psi_j|H_q|\psi_j\rangle \tag{5}$$

The contribution of ψ_1 is;

$$(V_{zz})_1 = 2\frac{1-C_R{}^2}{1+i_R{}^2}V_{p(z)} \tag{6}$$

where $V_{p(z)} = \langle\varphi_{p(z)}|H_q|\varphi_{p(z)}\rangle$ and $\langle\varphi_s|H_q|\varphi_{p(z)}\rangle = 0$, neglecting the two-center integral, $\langle\varphi_R|H_q|\varphi_R\rangle$, $\langle\varphi_{p(z)}|H_q|\varphi_R\rangle$, *etc.* as too small.

The contribution of $p(z)$ electrons in the molecular orbitals, ψ_2, ψ_3, and ψ_4, is;

$$\sum_{j=2}^{4}(V_{zz})_j = 6\frac{1-C_X{}^2}{1+i_X{}^2}V_{p(z)}\cos^2\alpha \tag{7}$$

Moreover, the contributions of the $p(x)$ and $p(y)$ electrons in ψ_2, ψ_3, and ψ_4 are;

$$\sum_{j=2}^{4}(V_{xx})_j = 3\frac{1-C_X{}^2}{1+i_X{}^2}V_{p(x)}\sin^2\alpha \tag{8}$$

and;

$$\sum_{j=2}^{4}(V_{yy})_j = 3\frac{1-C_X{}^2}{1+i_X{}^2}V_{p(y)}\sin^2\alpha \tag{9}$$

where $V_{p(x)} = \langle\varphi_{p(x)}|H_q|\varphi_{p(x)}\rangle$, *etc.*

If it is assumed that all of the $5p_x$, $5p_y$, and $5p_z$ orbitals have the same radial functions, the next equation is obtained:

$$V_{p(x)} = V_{p(y)} = -\frac{1}{2}V_{p(z)} \tag{10}$$

Consequently, the total field gradient, V_{zz}, is:

$$V_{zz} = 2V_{p(z)}\left[\frac{1-C_R{}^2}{1+i_R{}^2} + 3\frac{1-C_X{}^2}{1+i_X{}^2}\left(\frac{3\cos^2\alpha - 1}{2}\right)\right]$$

By introducing (2) and (3) into the above equation, we obtain:

$$\begin{aligned}
V_{zz} &= V_{p(z)}[(1-C_R{}^2)(1+I_R) - (1-C_R{}^2)(1+I_X)] \\
&= (1-C_R{}^2)(I_R - I_X)V_{p(z)}
\end{aligned} \tag{11}$$

where the bond ionic characters, I_X and I_R, are expressed as:

$$I_X = \frac{1-i_X{}^2}{1+i_X{}^2},\ I_R = \frac{1-i_R{}^2}{1+i_R{}^2}. \quad (I_X<0,\ I_R>0,\ |I_X|>|I_R|)$$

An analogus calculation for R_3SnX yields:

$$V_{zz}(R_3SnX) = (1-C_X{}'^2)(I_X{}' - I_R{}')V_{p(z)} \tag{12}$$

where C'_X is the coefficient included in one of the tin valence orbitals for R_3SnX, $(\varphi'_1 = C'_X\varphi_s + (1-C'_X{}^2)^{1/2}\varphi_{p(z)})$ and where I'_X and I'_R are the bond ionic characters for R_3SnX $(I'_X<0,\ I'_R>0,\ |I'_X|>|I'_R|)$.

By combining (11) with (12), we obtain:

$$\frac{V_{zz}(RSnX_3)}{V_{zz}(R_3SnX)} = -\frac{(1-C_R{}^2)(I_X - I_R)}{(1-C_X{}'^2)(I_X{}' - I_R{}')} \tag{13}$$

Since the rehybridization theory can be applied to $RSnX_3$ as well as to R_3SnX, it may be assumed that $C_R{}^2>1/4$ for $RSnX_3$ and $C_X{}'^2<1/4$ for R_3SnX. (This is exactly what Bent's rehybridization theory predicts.)

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Moreover, it is reasonable that we consider $|I'_X|>|I_X|$. For example, this consideration may be supported by the fact that the replacement of hydrogen by the more electronegative chlorine for chloromethanes, CH_nCl_{4-n}, makes the C–Cl bond less ionic.[16] As more direct evidence, we find, from the n.q.r. data for $(n\text{-}C_4H_9)_n\text{-}SnCl_{4-n}$ (n=0, 1, 2), that the replacement of chlorine atoms by buthyl groups leads to an increase in the ionic character in the Sn–Cl bond.[17] Other support is found in the recent calculation of orbital populations in aryltin chlorides.[18] Moreover, since I_R and I'_R are small compared to I_X and I'_X, $(I_X-I_R)/(I'_X-I'_R)\fallingdotseq I_X/I'_X$.[18] Therefore, it can be concluded that $|V_{zz}(RSnX_3)|<|V_{zz}(R_3SnX)|$ and that the more electronegative the substituents, X, the larger the field gradient, V_{zz}, for R_3SnX.

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