CHAPTER 6

MOSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS

CHAPTER-6

Introduction:

Mossbauer resonance have been observed for a number of nuclei including ^{119}Sn isotope having a relative abundance of 8.68%. This provides an excellent scope for using Mossbauer spectroscopy as a probe to study the nature of bonds and to determine the coordination number of the tin atom in organotin compounds. Although the interpretations of the experimental data, in most cases, are not entirely satisfactory, the Mossbauer technique has been quite extensively used in this field and a vast body of data on both isomer shifts and quadrupole splittings have already accumulated in chemical literature[1-4]. Goldanskii has suggested a linear relationship between the isomer shift and ligand electronegativity or percentage ionic character for tin tetrahalides. This view has been extended to other quadrivalent tin compounds by Cordy-Hayes and Herber and has been critically examined by Zuckerman[3,5,6]. Parish et al have shown that for SnX_4 and $SnX_4Y_2^{-2}$ type compounds (X, Y = F, Cl, Br or I) isomer shifts decrease with the increase in average electronegativity of the halogen atom and are essentially independent of the coordination number of the tin atom[7]. More over the relationship between isomer shift and tin proton spin-spin coupling constant[8] as well as a number of theoretical approaches to the calculation of isomer shifts in organotin compounds have been examined[9,10]. It has

been suggested that the imbalance in the Π-interactions determines whether or not a quadrupole splitting would be observable in organotin compounds[11,12]. This rule is however only qualitative in nature and even fails in many cases[11,13-15]. Greenwood et al have obtained a correlation between quadrupole splitting and the occupation number of the three individuals 5p orbitals of the tin atom calculated by SCF MO method of Pople with basis set involving tin 5s, 5p and 5d orbitals[9]. More recently the imbalance in the tin-ligand σ-bond polarities has been suggested as the dominating factor in determining the quadrupole splittings and a good correlation between the inductive Taft constant[17] and the quadrupole splittings has been obtained for a number of organotin compounds[4]. However, inspite of considerable attention given in this field, no general approach of wide applicability has yet been developed for the interpretation and correlation of the Mossbauer parameters in organotin compounds.

Theoretically the ^{119}Sn isomer shifts are linearly related to the total electron density at the tin nucleus[18] which in turn is related to the s-and p-electron populations in the valence shell[10,19], while the quadrupole splitting depends on the magnitude of the field gradient[18] which is related to the asymmetry of the p-electron distribution in the valence p-orbitals of the tin atom. Thus, in order to investigate the Mossbauer isomer shifts and quadrupole splittings in organotin compounds the knowledge of the electron population at the tin 5s, $5p_x$, $5p_y$ and $5p_z$ orbitals are essential. Although a number of sophisticated quantum mechanical procedures like SCF MO

etc. are available for this purpose, such methods are of little value to experimental chemists as a general tool for the interpretation of the Mossbauer data because of the tedious calculations and the complicated mathematics involved therein.

In the present chapter we have, therefore, developed an extremely simple, yet very effective, method for this purpose.

In the localized MO approach, the s- and p-electron populations at the tin atom may be easily calculated from the co-efficients of the bonding MO provided the s- and p character of the hybridised valence orbitals of the tin atom are known. In the Del Re method, atomic orbitals are not clearly defined. As such the s- and p-content of the hybridised orbitals of the tin atom used for the formation of σ-bonds with the ligand orbitals are not directly available from the solutions of the secular equations used in the Del Re procedure. However, a clue to the s-character of a tin-carbon bond may be obtained from the correlation between the calculated Del Re Coulomb integral parameter and J(Sn-C-H) spin-spin coupling constants in organotin compounds discussed in Chapter 5. In the current chapter we will first develop a simple method of estimating s- and p-character of the different bonds formed by the tin atom from Del Re parameters and then use these data to calculate populations in the valence shell of the tin atom. The electron density at the tin nucleus has then been obtained by using the formula obtained by Lees and Flinn from an analysis of the SCF AO's of the tin-atom[19].

The calculated electron densities show a fair correlation with the experimental Mossbauer isomer shifts in a number of organo-

tin compounds and the value of $(\Delta R/R)$ calculated from the slope of the correlation line is 3.2×10^{-4} in excellent agreement with the value of 3.3×10^{-4} obtained from an independent method based on internal electron conversion measurements[20]. Moreover a method for calculating the asymmetry in the p-electron distribution at the tin atom has been developed and an asymmetry parameter 'A' has been defined. This parameter shows an excellent correlation with the experimental quadrupole splittings.

(A) Mossbauer isomer shifts in organotin compounds:

Method: Mossbauer isomer shift in an organotin compound relative to a standard source is given by eqn. (6-1)[3,18] where $(\Delta R/R)$ is the fractional change in the nuclear charge radius of the tin atom on excitation;

$$\delta = C. (\Delta R/R)[\psi_a^2(o) - \psi_s^2(o)] \qquad (6\text{-}1)$$

$\psi_a^2(o)$ and $\psi_s^2(o)$ represents the electron density at the nucleus of the absorber and the source respectively, and C is a constant given by eqn. (6-2)

$$C = 4/5\pi e^2 Z R^2 \qquad (6\text{-}2)$$

Here R is the equivalent radius in the uniformly charged sphere approximation, Z is the atomic number of the Mossbauer active nucleus and e is the electronic charge.

Using relativistic wave functions for the tin atom in various oxidation states and different electronic configurations, Lees and Flinn[19] have shown that $\psi_a^2(o)$, in units of a_o^{-3*} is given by the eqn. (6-3) where ρ_o represents the electron density of the

$$\psi_a^2(o) = \rho_o + \rho \qquad (6\text{-}3)$$

bare core state (Sn^{4+}), and ρ is the electron density due to the valence electron which is given by eqn. (6-4) ** where n_s and n_p

$$\rho = n_s\ (\phi_s + \Delta_s + S_{ss}.n_s + 2S_{sp}.n_p) \qquad (6\text{-}4)$$

are the s- and p-electron population ϕ_s is the charge density of a single 5s electron, Δ_s is the inner screening of a single 5s electron, S_{ss} is the 5s-5s screening effect and S_{sp} is the 5s-5p screening effect. The calculated values of ϕ_s , Δ_s, S_{ss} and S_{sp} are 58.28, -1.00, -3.77 and -1.65 respectively[19] in units of a_o^{-3}. Substituting these values in eqn. (6-4) we have eqn. (6-5).

$$\rho = n_s\ (57.28 - 3.77n_s - 3.30n_p)a_o^{-3} \qquad (6\text{-}5)$$

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* a_o is the atomic units of length, i.e. 0.529A^o.

** Though, only the s-electrons have definite probability at the nucleus of an atom, the p-electrons exert an indirect influence on the electron density at the nucleus by screening the s-electron.

Substituting the value of $\psi_a^2(o)$ and $\psi_s^2(o)$ from eqn. (6-3) in eqn. (6-1), the isomer shift δ will be given by the eqn. (6-6) where the primed term indicate the source. The electron density of the bare core state (Sn^{4+}core) being a constant, i.e. $\rho_o = \rho_o'$, eqn. (6-6) simplifies to eqn. (6-7) where the term $-C.(\Delta R/R)\rho'$ has

$$\delta = C(\Delta R/R)[(\rho_o + \rho) - (\rho_o' + \rho')] \qquad (6\text{-}6)$$

$$\delta = C.(\Delta R/R)(\rho - \rho')$$
$$= C.(\Delta R/R)\rho + C' \qquad (6\text{-}7)$$

been replaced by C'. Since C and $(\Delta R/R)$ are constants, the value of C' depends on the value of ρ' i.e. the source only. If the isomer shifts are expressed relative to a standard source, C' may then be treated as a constant. Therefore, the isomer shifts relative to a fixed source will be linearly related to ρ, which may be calculated from the s- and p-electron populations of the valence shell by eqn. (6-5). In the following section we would, therefore, develop a simple method of calculating the quantities n_s and n_p by the Del Re method.

Consider a tetravalent tin compound. The ith hybridised valence orbital ψ_i, which forms the ith σ-bond with the ligand, may be written as in eqn. (6-8) where s, p_x, p_y and p_z represents the atomic orbitals of the tin atom in the valence shell. The ith localized bonding MO, ϕ_i, formed from the tin orbital ψ_i and the

ligand orbital ψ_X may be written as in eqn. (6-9). Hence the electron population, n_j, in the jth atomic orbital (j = s, p_x, p_y or p_z) of the tin atom will be given by eqn. (6-10) where the factor 2 has been introduced to account for the fact that every bonding MO is occupied by two electrons.

$$\psi_i = a_{is}\cdot s + a_{ix}\cdot p_x + a_{iy}\cdot p_y + a_{iz}\cdot p_z \qquad (6\text{-}8)$$

$$\phi_i = C_i\cdot\psi_i + C_X\cdot\psi_X \qquad (6\text{-}9a)$$

$$= C_i\cdot a_{is}\cdot s + C_i a_{ix}\cdot p_x + C_i a_{iy}\cdot p_y + C_i\cdot a_{iz}\cdot p_z + C_X\cdot\psi_X \qquad (6\text{-}9b)$$

$$n_j = 2\sum_i C_i^2\cdot a_{ij}^2 \qquad (6\text{-}10)$$

Because the Del Re bond charge Q_{Sni}, for the ith tin ligand bond is given by eqn. (6-11) and the total number of bonds formed by the

$$Q_{Sni} = 1 - 2C_i^2 \qquad (6\text{-}11)$$

tin atom is four in the present case, the total electron population N at the tin atom will be given by eqn. (6-12), where q_{Sn} ($=\sum_i Q_{Sni}$) is the partial charge at the tin atom. Similarly the s-electron population n_s and the total p-electron population n_p in the valence shell of the tin atom will be given by eqns. (6-13) and (6-14) respectively where a_{is}^2 has been replaced by λ_{si}, the s character

$$N = \sum 2C_i^2 = \sum_i (1-Q_{Sni}) = 4-q_{Sn} \qquad (6\text{-}12)$$

$$n_s = \sum 2\, c_i^2 . a_{is}^2 = \sum_i (1 - q_{Sni}) . \lambda_{si} \qquad (6\text{-}13)$$

$$n_p = N - n_s = 4 - q_{Sn} - \sum_i (1 - q_{Sni}) . \lambda_{si} \qquad (6\text{-}14)$$

of the ith hybridised valence orbital of the tin atom. Thus n_s and n_p can be evaluated if the values of λ_{si} can be determined. In the previous chapter it has been shown that for Me_nSnX_{4-n} (all X's identical) type compounds the s-character λ_s, of the tin orbital used to bond the methyl group is given by eqn. (6-15) and the tin proton spin-spin coupling constant, $J(^{119}Sn\text{-}C\text{-}H)$, is given by eqn. (6-16)[21]. The value of K can be readily determined from the slope

$$\lambda_s = 0.25 + K \sum(\delta_X - \delta_{Sn})/n \qquad (6\text{-}15)$$

$$J(^{119}Sn\text{-}C\text{-}H) = 0.25B + K.B \sum (\delta_X - \delta_{Sn})/n \qquad (6\text{-}16)$$

and intercept of the correlation line of J(Sn-C-H) and $\sum(\delta_X - \delta_{Sn})/n$. Using a value of 0.284 for K*, calculated from the correlation line

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* A much different value of K is obtained if one considers the correlation line of the ethyl compounds given in Fig. (5-5). Because of considerable discrepancies in the reported values of $J(^{119}Sn\text{-}C\text{-}H)$ in the ethyl compounds (values as low as 32.2 Hz and as high as 69.2 Hz have been reported for Et_4Sn[2]) these data appear to be unreliable for the evaluation of K. The fact that the value of K obtained from Me_nSnX_{4-n} type compounds is applicable also to many other organotin compounds containing propyl, butyl, benzyl groups indicates beyond doubt that the J(Sn-C-H) data for the ethyl compounds include large systematic errors.

shown in Fig. (5-4), eqn. (6-15) reduces to eqn. (6-17).

$$\lambda_s = 0.25 + 0.284\ (4-n)(\delta_X - \delta_{Sn})/n \qquad (6\text{-}17)$$

As λ_s is the fractional s-character of each of the tin orbitals used to bond the methyl groups, the remaining s-character, i.e., $(1 - n\lambda_s)$, will be equally distributed between the remaining (4-n) tin orbitals used to bond (4-n) identical ligands, X. Therefore the fractional s-character of each of the tin orbitals involved in the Sn-X bond is $(1 - n\lambda_s)/(4-n)$. With these values of λ_s, eqn. (6-13) simplified to eqn. (6-18)

$$n_s = n(1 - Q_{SnC}).\lambda_s + (1 - n.\lambda_s)(1 - Q_{SnX}) \qquad (6\text{-}18)$$

All the parameters involved in eqn. (6-17) and (6-18) are available from the Del Re calculations. Thus, n_s and hence n_p [eqn. (6-14)] may be easily calculated. Although eqn. (6-17) has been derived by considering Me_nSnX_{4-n} type compounds only, we assume that the relation is true for all R_nSnX_{4-n} type compounds as long as $\delta_X > \delta_{C(R)}$. It is necessary to impose this condition since eqn. (6-15) has been derived from the isovalent hybridisation rule[22] by assuming that the electronegativity of the ligand X is greater than that of the carbon atom bonded to the tin atom (see Chapter 5). This assumption is justified by the fact that (i) for a number of R_nSnX_{4-n} type compounds (R = Me, Pr, Bz etc.) the reported values of $J(^{119}Sn\text{-}C\text{-}\overset{\alpha}{H})$ are of comparable magnitude[2] which should be the case only if

eqns. (6-16) and (6-17) are applicable to all these compounds and (ii) fair correlations are obtained between the calculated parameters and the experimental Mossbauer isomer shifts and quadrupole splittings in such cases also.

Result and discussion:

For the present study we have selected a number of compounds of the type R_nSnX_{4-n} only (the eqns. derived in the present chapter is applicable to such cases only) where n = 0 to 4, R = Me, Bu, Ph, $PhC(Me_2)CH_2$ and X = Cl, CF_3, C_6F_5, Ph and Vi group for which the necessary Del Re parameters have been evaluated. The calculated values of $\lambda_{s(C)}$, $\lambda_{s(X)}$, δ_X, δ_{Sn} and δ_C for these compounds are given in Table (6-1). $\lambda_{s(C)}$ and $\lambda_{s(X)}$ stand for the s-characters of

Table 6-1

Calculated s-character $\lambda_{s(C)}$ and $\lambda_{s(X)}$ of Sn-C(R) and Sn-X bond and the Coulomb integral parameters $\delta_{C(R)}$, δ_X and δ_{Sn} in some R_nSnX_{4-n} type compounds where n = 0 to 4, R = Me, Bu, Ph, $PhC(Me_2)CH_2$-, and X = Cl, CF_3, C_6F_5, Ph and Vi groups.

Compound	$\lambda_{s(C)}$	$\lambda_{s(X)}$	$\delta_{C(R)}$	δ_X	δ_{Sn}
Me_4Sn	0.250	-	0.1000	-	-0.0600
Me_3SnCl	0.283	0.151	0.1098	0.3513	0.0032
Me_2SnCl_2	0.336	0.164	0.1212	0.3805	0.0764

Contd..

Table 6-2(Contd.)

Compound	$\lambda_{s(C)}$	$\lambda_{s(X)}$	$\delta_{C(R)}$	δ_X	δ_{Sn}
Bu_4Sn	0.250	-	0.1002	-	-0.0599
Bu_3SnCl	0.283	0.151	0.1085	0.3511	0.0027
Bu_2SnCl_2	0.337	0.163	0.1184	0.3803	0.0758
$BuSnCl_3$	0.466	0.178	0.1299	0.4147	0.1617
Me_3SnCF_3	0.277	0.169	0.1023	0.2438	-0.0450
$Me_3Sn(C_6F_5)$	0.270	0.190	0.1009	0.1580	-0.0539
$Me_2Sn(C_6F_5)_2$	0.309	0.191	0.1018	0.1586	-0.0479
$MeSn(C_6F_5)_3$	0.421	0.193	0.1027	0.1592	-0.0419
$Sn(C_6F_5)_4$	-	0.250	-	0.1598	-0.0361
Me_3SnPh	0.269	0.193	0.1007	0.1491	-0.0548
Me_3SnVi	0.269	0.193	0.1008	0.1504	-0.0547
Ph_4Sn	0.250	-	0.1506	-	-0.0397
Ph_3SnCl	0.282	0.154	0.1566	0.3573	0.0184
Ph_2SnCl_2	0.335	0.165	0.1635	0.3846	0.0865
$PhSnCl_3$	0.463	0.179	0.1718	0.4169	0.1673
*$(Neo)_4Sn$	0.250	-	0.1003	-	-0.0599
*$(Neo)_3SnCl$	0.284	0.148	0.1087	0.3612	0.0028
$SnCl_4$	-	0.250	-	0.4559	0.2647

*Neo = $PhC(Me_2)CH_2^-$

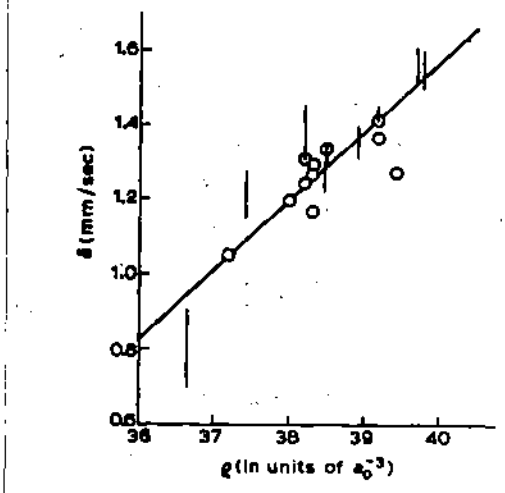

Fig. (6-1) Correlation between the calculated electron density ρ and the experimental isomer shift, δ .

the tin orbitals directed towards the carbon atom of the group R and the ligand X respectively. The calculated values of n_s, n_p and ρ, obtained from eqns. (6-13), (6-14) and (6-5) along with the observed isomer shifts[1-3] are given in Table (6-2). Fig. (6-1) shows

Table 6-2

Calculated values of the electron population n_s and n_p and the experimental Mossbauer isomer shifts.

Compound	n_s	n_p	ρ in a_o^{-3}	δ (mm/sec.) relative to SnO_2
Me_4Sn	0.840	2.520	38.48	1.22 - 1.29
Me_3SnCl	0.851	2.442	39.15	1.41 - 1.44
Me_3SnCF_3	0.829	2.440	38.22	1.31
$Me_3Sn(C_6F_5)$	0.834	2.489	38.30	1.27
Me_3SnPh	0.835	2.495	38.32	1.16
Me_3SnVi	0.835	2.493	38.33	1.30
Me_2SnCl_2	0.859	2.375	39.69	1.52 - 1.61
$Me_2Sn(C_6F_5)_2$	0.829	2.459	38.18	1.25
$MeSn(C_6F_5)_3$	0.823	2.429	37.99	1.19
Bu_4Sn	0.840	2.520	38.48	1.30 - 1.35
Bu_3SnCl	0.852	2.444	39.19	1.36, 1.58-1.65
Bu_2SnCl_2	0.861	2.377	39.77	1.50 - 1.60
$BuSnCl_3$	0.865	2.324	40.10	1.31, 1.70
Ph_4Sn	0.810	2.429	37.43	1.15 - 1.27
Ph_3SnCl	0.825	2.384	38.19	1.31 - 1.45
Ph_2SnCl_2	0.839	2.345	38.91	1.31 - 1.38

Contd..

Table 6-2 (Contd.)

Compound	n_s	n_p	ρ in a_o^{-3}	δ (mm/sec.) relative to SnO_2
$PhSnCl_3$	0.849	2.314	39.43	1.27
*$(Neo)_4Sn$	0.840	2.519	38.88	1.34
*$(Neo)_3SnCl$	0.851	2.433	39.18	1.41
$(C_6F_5)_4Sn$	0.804	2.412	37.21	1.04
$SnCl_4$	0.788	2.362	36.66	0.7 - 0.9

*Neo = $PhC(Me_2)CH_2^-$

the correlation between the calculated electron density, ρ and the experimental isomer shifts. In view of the large discrepancies in the reported isomer shifts no meaningful choice of the data is possible and the complete range, wherever available, is shown in Fig. (6-1). In a few cases (e.g. $BuSnCl_3$ δ = 1.31 & 1.70 mm/sec) the discrepancy between the values reported by different worker is so large that these points had to be left out. Considering such large discrepancies in the experimental data the correlation between ρ and the isomer shift is very satisfactory and barring only two cases out of a total of 21 compounds given in Table (6-2) the deviation of the experimental data from the correlation line is less than $\pm$0.05 mm/sec; the reported uncertainity in the isomer shift data being of the order of $\pm$ 0.1 mm/sec[1]. This clearly demonstrates the wide applicability as well as realiabity of the present method.

As a further stringent test of the reliability we have calculated the value of $(\Delta R/R)$ from the slope of the correlation line, which, according to eqn. (6-7) is $C(\Delta R/R)$. Expressing the isomer shift in mm/sec and using the value of R as $1.24 \times A^{1/3} \times 10^{-13}$ cm. (A = 119 in the present case) given by Anderson et al[23] this constant C is calculated to be 0.85×10^{-22} for 23.8 keV Mossbauer transition of tin from eqn. (6-2). Using this value of C, $(\Delta R/R)$ is found to be 3.2×10^{-4} from the slope of the correlation line given in Fig. (6-1). This value, though in excellent agreement with the value of 3.3×10^{-4} obtained from an independent method based on internal electron conversion[20], differs by a factor of about 3 from that obtained by Lees and Flinn[19]. We, however, consider the present calculations, though apparently crude in nature, to be more reliable because (i) the reliability of the Del Re calculations and the various parameters involved in the present calculations have been already demonstrated by the very successful interpretation of many other properties of organotin compounds as indicated in the earlier chapters[21,24-29]; (ii) no assumption of doubtful validity (except those inherent in the Del Re approximations) is involved in the calculation of electron density as is the case with most other methods*, (iii) the calculated asymmetry

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*For example Lees and Flinn[19] considered the bonding in $(SnF_6)^{2-}$ to be purely ionic with an ideal Sn^{4+} central ion which is very

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in the electron distribution at the tin atom, to be discussed in the following section, shows a good quantitative correlation with the experimental quadrupole splittings. The excellent agreement between our value of ($\triangle R/R$) and that obtained by the direct method[20] further supports our contention.

(B) Quadrupole splittings in organotin compounds:

Method: The Mossbauer quadrupole splitting in a compound depends on the magnitude of the electric field gradient at the nucleus of the absorber. In a tetravalent tin compound the electric field gradient is due to (i) asymmetry in the distribution of the p-electrons between the three p-orbitals and/or (ii) asymmetric distribution of the charges of the ligand atoms[18]. The existence of a good linear relation between the inductive Taft[17] constant and quadrupole splittings in a number of organotin compounds indicate the asymmetry in the p-electron distribution to be the dominating factor[4]. In the preceding section we have already shown that the total p-electron

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(Contd.-)
doubtful since the possibility of considerable covalent character can not be excluded. Similarly the calculation of the isomer shift for ideal $5s^2$ configuration by extrapolation to zero quadrupole splitting may be in error in view of our discussion on quadrupole splitting and asymmetry. In fact, consideration of these effects will tend to increase the value of ($\triangle R/R$), even if calculated by their method.

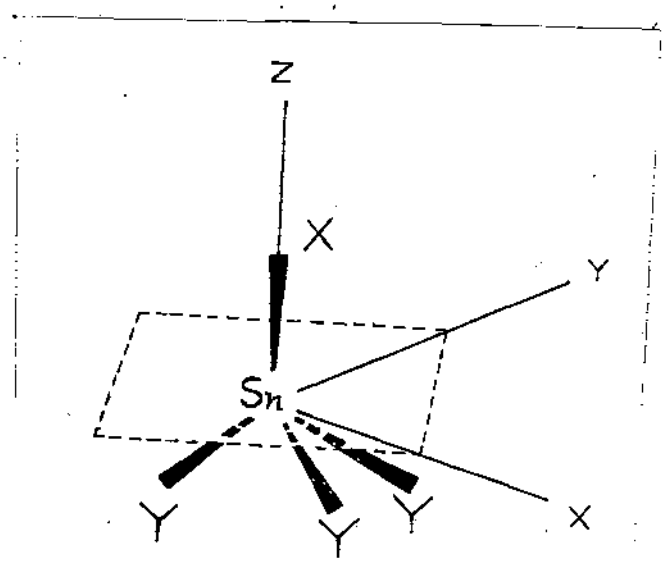

Fig. (6-2) Choice of co-ordinates in Y_3SnX type compounds.

population, n_p at the tin atom in tetravalent tin compounds can be calculated by eqn. (6-14). In order to evaluate the asymmetry of the p-electron distribution it is necessary to know the population of the three individual 5p obbitals of the tin atom. To obtain quantitative correlation between the asymmetry in the p-electron distribution and the quadrupole splittings we, therefore, develop a method of calculating the electron population in different p-orbitals, of the tin atom and then define an asymmetry parameter capable of expressing quantitatively the deviation of the calculated electron distribution from spherical aymmetry.

Compounds of the type Y_3SnX belong to C_{3v} point group. The four hybrid orbitals, ψ_1, ψ_2, ψ_3 and ψ_4, expressed as in eqns. (6-19a) to (6-19d) forms four σ-bonds with the ligands Y and X. Let us now consider that the hybrid orbital ψ_1 forms the bond with the ligand X. The Z axis is conventionally chosen along the

$$\psi_1 = a_{1s}\cdot s + a_{1x}\cdot p_x + a_{1y}\cdot p_y + a_{1z}\cdot p_z \qquad (6\text{-}19a)$$

$$\psi_2 = a_{2s}\cdot s + a_{2x}\cdot p_x + a_{2y}\cdot p_y + a_{2z}\cdot p_z \qquad (6\text{-}19b)$$

$$\psi_3 = a_{3s}\cdot s + a_{3x}\cdot p_x + a_{3y}\cdot p_y + a_{3z}\cdot p_z \qquad (6\text{-}19c)$$

$$\psi_4 = a_{4s}\cdot s + a_{4x}\cdot p_x + a_{4y}\cdot p_y + a_{4z}\cdot p_z \qquad (6\text{-}19d)$$

Sn-X bond direction, coincident with the C_3 axis of the molecule [Fig. (6-2)]. With this choice of axis and using normalization

condition (eqn. 6-19e), the coefficients a_{iz}'s of the hybrid

$$a_{is}^2 + a_{ix}^2 + a_{iy}^2 + a_{iz}^2 = 1 \qquad (6\text{-}19e)$$

orbitals ψ_1, ψ_2, ψ_3 and ψ_4 may be determined as follows.

Since both p_x and p_y orbitals have zero amplitude along the z-axis, $a_{1x} = a_{1y} = 0$. Therefore the orbital ψ_1 may be rewritten as in eqn. (6-20) and the coefficients will be given by eqn. (6-21). The value of the coefficient a_{1z} is thus obtained from eqn. (6-22)

$$\psi_1 = a_{1s}s + a_{1z}\cdot p_z \qquad (6\text{-}20)$$

$$a_{1s}^2 + a_{1z}^2 = 1 \qquad (6\text{-}21)$$

$$a_{1z} = (1 - a_{1s}^2)^{\frac{1}{2}} \qquad (6\text{-}22)$$

Evidently the remaining p_z character, $1-a_{1z}^2$, will be equally distributed among the three remaining orbitals ψ_2, ψ_3 and ψ_4 because of symmetry so that:

$$a_{2z}^2 = a_{3z}^2 = a_{4z}^2 = (1- a_{1z}^2)/3$$

$$= a_{1s}^2/3 \qquad (6\text{-}23)$$

It is obvious from eqns. (6-22) and (6-23) that the p_z character of the orbitals ψ_1, ψ_2, ψ_3 and ψ_4 can be computed from the s-character of the orbital, ψ_1. Using these values of a_{iz}^2 in eqn. (6-10)

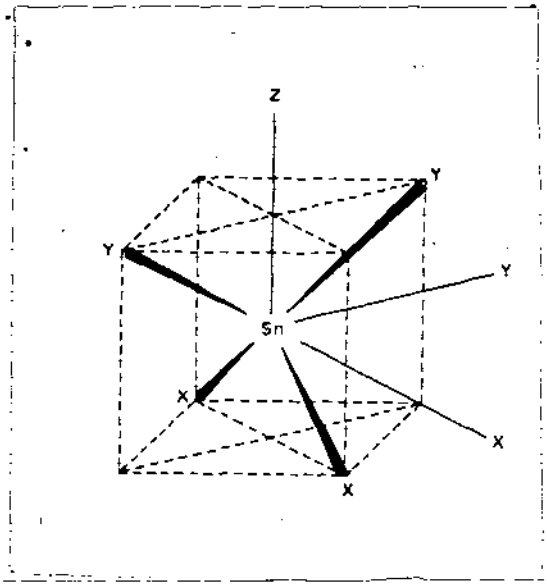

Fig. (6-3) Choice of co-ordinates in Y_2SnX_2 type compounds.

along with eqn. (6-11) it is easy to show that the population of the p_z orbital, n_z, will be given by eqn. (6-24) where a_{is}^2 has been replaced λ_{sX}. Since λ_{sX} can be computed by using eqn. (6-17) and

$$n_z = 1 + \lambda_{sX}(Q_{SnX} - Q_{SnY}) - Q_{SnX} \qquad (6\text{-}24)$$

all other quantitites are available by standard Del R_e calculations, n_z may be easily obtained. Further, because of the axial symmetry in Y_3SnX molecules the population of the p_x and p_y orbitals, n_x and n_p will be equal and are thus given by eqn. (6-25)

$$n_x = n_y = (n_p - n_z)/2 \qquad (6\text{-}25)$$

For molecules of the type Y_2SnX_2 belonging to C_{2v} point group a different method is needed. For this purpose the z-axis may be chosen along the C_2 axis and the x and y axes are chosen along the mutually perpendicular SnX_2 and SnY_2 planes respectively as shown in Fig. (6-3). With this choice of axes and using the normalization and orthogonality conditions, the four hybridized valence orbital of the tin atom ψ_1, ψ_2, ψ_3 and ψ_4 may be writen as in eqns. (6-26a) to (6-26d) where the superscripts refer to the plane on which the orbitals are located.*

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*Deduction of hybrid orbital with this choice of axes is given in Appendix I.

$$\psi_1^{xz} = a.s + (1/2)^{\frac{1}{2}}.p_x + (\tfrac{1}{2} - a^2)^{\frac{1}{2}}.p_z \qquad (6\text{-}26a)$$

$$\psi_2^{xz} = as - (\tfrac{1}{2})^{\frac{1}{2}}.p_x + (\tfrac{1}{2} - a^2)^{\frac{1}{2}}.p_z \qquad (6\text{-}26b)$$

$$\psi_3^{yz} = (\tfrac{1}{2} - a^2)^{\frac{1}{2}}.s + (\tfrac{1}{2})^{\frac{1}{2}}.p_y - a.p_z \qquad (6\text{-}26c)$$

$$\psi_4^{yz} = (\tfrac{1}{2} - a^2)^{\frac{1}{2}}.s - (\tfrac{1}{2})^{\frac{1}{2}}.p_y - a.p_z \qquad (6\text{-}26d)$$

Substituting the values of the appropriate coefficients from eqns. (6-26a) - (6-26d) in eqn. (6-10) and using eqn. (6-11), it is easy to show that the population of the different 5p orbitals of the tin atom will be given by eqns. (6-27) - (6-29). Thus, the p-electron distributions in all organotin compounds of the type R_nSnX_{4-n}

$$n_x = (1 - Q_{SnX}) \qquad (6\text{-}27)$$

$$n_y = (1 - Q_{SnY}) \qquad (6\text{-}28)$$

$$n_z = 1 + 2\lambda_{SX}.(Q_{SnX} - Q_{SnY}) - Q_{SnX} \qquad (6\text{-}29)$$

($n = 1$, 2 or 3) may be computed from the data obtained by simple Del Re calculations.

Since the electric field gradient is determined by the deviation from the spherical symmetry it is now necessary to define a parameter capable of expressing this deviation quantitatively. For spherical symmetry each of the three p-orbitals should have equal number of electrons, and therefore the deviation from spherical

symmetry may be defined as the root mean square deviation of the actual electron population from the hypothetical spherically symmetric distribution. If the total number of p-electrons were equally distributed the population of each of the orbitals would have been $n_p/3$. Hence the root mean square deviation from the spherical symmetry will be given by eqn. (6-30). We will refer to the parameter A

$$A = \left[(n_p/3 - n_x)^2 + (n_p/3 - n_y)^2 + (n_p/3 - n_z)^2\right]^{\frac{1}{2}} \qquad (6\text{-}30)$$

in eqn. (6-30) as the asymmetry parameter which should not be confused with the conventional asymmetry parameter $\eta \left[= (V_{xx} - V_{yy})/V_{zz}\right]$[18].

Result and Discussion:

The total p-electron population, n_p, is calculated by the use of eqn. (6-14); the electron populations n_x, n_y and n_z are then calculated either by eqns. (6-24) and (6-25) or by the eqns. (6-27), (6-28) and (6-29) depending on whether the molecule belongs to the point group C_{3v} or C_{2v} and finally the asymmetry parameter A is calculated from eqn. (6-30). The calculated values of n_x, n_p, n_z and the asymmetry parameter A for a number of organotin compounds of the type R_nSnX_{4-n} (n = 1, 2 or 3) are given in Table (6-3) along with the reported quadrupole splittings. It has already been mentioned that the quadrupole splitting depends both on the asymmetry in the p-

Table 6-3

Calculated values of the electron population of the p_x, p_y and p_z orbitals of tin, the asymmetry parameter, A, and the experimental quadrupole splittings.

Compound	n_x	n_y	n_z	A	ΔE_Q (mm/sec.)
Me_3SnCl	0.893	0.893	0.656	0.1935	3.01 - 3.41
Me_2SnCl_2	0.955	0.662	0.758	0.2114	3.33 - 3.55
Bu_3SnCl	0.895	0.895	0.655	0.1955	2.78 - 3.40
$BuSnCl_3$	0.719	0.719	0.886	0.1364	1.83
Ph_3SnCl	0.862	0.862	0.660	0.1649	2.45 - 2.56
Ph_2SnCl_2	0.923	0.669	0.753	0.1831	2.66 - 2.90
$PhSnCl_3$	0.723	0.723	0.869	0.1196	1.80 - 1.84
Me_3SnCF_3	0.853	0.853	0.735	0.0959	1.38
*$(Neo)_3SnCl$	0.894	0.894	0.645	0.2033	2.63
$MeSn(C_6F_5)_3$	0.799	0.799	0.832	0.0274	1.14
$Me_2Sn(C_6F_5)_2$	0.850	0.794	0.815	0.0405	1.48 -1.56
$Me_3Sn(C_6F_5)$	0.845	0.845	0.799	0.0376	1.31
$PhSn(C_6F_5)_3$	0.803	0.803	0.809	0.0049	0.92
$Ph_2Sn(C_6F_5)_2$	0.811	0.802	0.805	0.0063	1.11
$Ph_3Sn(C_6F_5)$	0.811	0.811	0.803	0.0061	0.90 - 0.98

Contd..

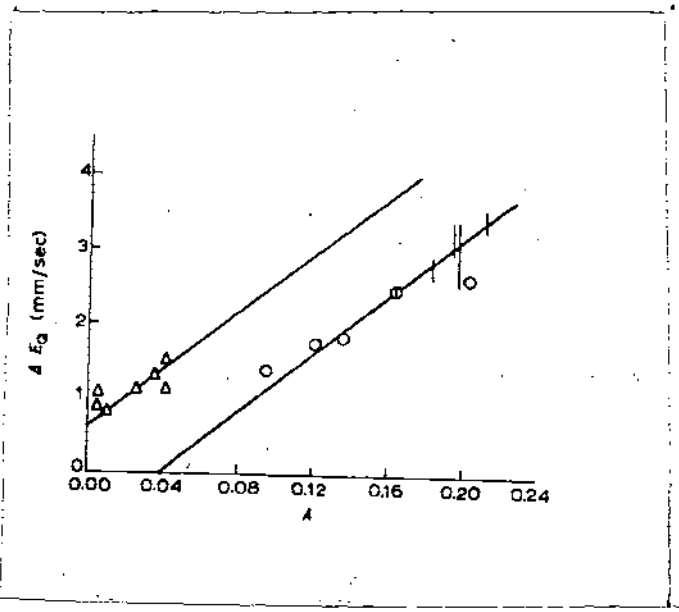

Fig. (6-4) Correlation between the calculated asymmetry parameter A and the experimental quadrupole splitting, ΔE_Q.

Table 6-3 (Contd..)

Compound	n_x	n_y	n_z	A	ΔE_Q (mm/sec.)
$Me_3Sn(C_6Cl_5)$	0.846	0.846	0.794	0.0421	1.09
$Ph_3Sn(C_6Cl_5)$	0.811	0.811	0.798	0.0106	0.84
$(C_6F_5)_3Sn(C_6H_4Me\text{-}p)$	0.803	0.803	0.809	0.0049	1.02
$(C_6F_5)_2Sn(C_6H_4Me\text{-}p)_2$	0.811	0.802	0.805	0.0063	1.18

* Neo = $PhC(Me)_2CH_2^-$

electron distribution at the tin atom and the asymmetry in the ligand charge distribution. As such linear correlation between the parameter A and quadrupole splittings should be expected only if asymmetry due to the charge distribution of the ligands is either very small or constant or varies consistently with the parameter A. Fig. (6-4) shows that the compounds given in Table (6-3) fall into two groups. All compounds for which X = Cl or CF_3 fall on one straight line and those for which X is C_6F_5 or C_6Cl_5 fall on the other line.

The linearity of the relation between A and the quadrupole splitting and the presence of intercepts indicate that the asymmetry due to ligand charge distribution around the central tin atom exert

nearly constant influence on the field gradient in a given series. Both the lines shown in Fig. (6-4) have equal slopes, suggesting that the main difference between the two groups of compounds is the magnitude of the asymmetry arising from the substitutents. In the case of R_nSnX_{4-n} compounds with X = C_6F_5 or C_6Cl_5, R = alkyl, Ph or pMe - $C_6H_4^-$, Fig. (6-4) shows that the correlation line has a relatively large intercept suggesting large contribution to the total quadrupole splitting from the asymmetry in the charge distributions on the substituent. When X is Cl or CF_3, this contribution is very small and the correlation line meets the x-axis, representing the asymmetry parameter A at about 0.04. It is interesting to note that all R_nSnX_{4-n} type compounds, where R = alkyl, Ph or Vi and X = Vi, Ph or p-substituted phenyl group for which A is less than 0.04 do not show any quadrupole splitting. The calculated values of n_x, n_p and n_z along with A for a few such compounds are shown in Table (6-4). This seems to be a general rule, the only exception

Table-6-4

Calculated electron population of the p_x, p_y and p_z orbitals and the asymmetry parameter, A, for some organotin compounds showing no quadrupole splitting.

Compound	n_x	n_y	n_z	A
Me_3SnVi	0.844	0.844	0.805	0.0318
Me_3SnPh	0.845	0.845	0.805	0.0327

Contd..

Table 6-4 (Contd.)

Compound	n_x	n_y	n_z	A
$Me_3Sn(C_6H_4F\text{-}p)$	0.845	0.845	0.805	0.0327
Ph_3SnVi	0.810	0.810	0.809	0.0014
$PhSnVi_3$	0.809	0.809	0.810	0.0010

being compounds having O-substituted phenyl groups. In these cases, the quadrupole splitting is mainly due to the asymmetric charge distribution associated with such substituents as is demonstrated by the relatively large intercept in the correlation line. As a further test of the validity of this correlation we have made some provisional calculations on $R_3SnC \equiv CX$ type compounds which show quadrupole splitting.

For compounds of the type $R_3SnC \equiv CX$ having sp carbon atoms the necessary Del R_e parameters have not been evaluated so far. However, in Chapter 1 it has been shown that the inductive parameters do not change from sp^3 to sp^2 carbon[24]. We, therefore, assume that the same set of inductive parameters would be applicable to sp-carbon atom also. On the other hand, the parameter δ° is approximately proportional to electronegativity. The electronegativity of the carbon atom increases as the hybridisation changes from sp^3 to

sp^2 to sp^{30}. Thus, on the basis of δ° values of sp^3 and sp^2 carbon (0.70 and 0.12 respectively) $\delta^\circ_{C(sp)}$ is likely to be of the order of 0.22. Using this value, Del Re calculations have been carried out for some $R_3SnC \equiv CX$ type compounds in the usual way. The results are given in Table (6-5) along with the experimental quadrupole splittings. Data given in Table (6-5) show that for $R_3SnC \equiv CX$

Table 6-5

Calculated values of n_s, n_x, n_y, n_z, A and the observed quadrupole splitting ΔE_Q of some $R_3SnC \equiv CX$ (R = Me or Et, X = H, Me, Et, Ph or Cl) type compounds using a provisional value of 0.22 for $\delta^\circ_{C(sp)}$.

Compound	n_s	n_x	n_y	n_z	A	ΔE_Q (mm/sec.)
$Me_3SnC \equiv CPh$	0.829	0.853	0.853	0.737	0.0943	1.17
$Et_3SnC \equiv CH$	0.829	0.853	0.853	0.737	0.0943	1.48
$Et_3SnC \equiv CMe$	0.829	0.853	0.853	0.737	0.0943	1.22
$Et_3SnC \equiv CPh$	0.829	0.852	0.852	0.737	0.0943	1.42
$Et_3SnC \equiv CCl$	0.829	0.853	0.853	0.730	0.1000	1.75

(R = Me, Et; X = H, Me, Et, Ph or Cl) type compounds the asymmetry parameter A lies in the range of 0.09 - 0.10 and the reported quadrupole splittings fall close to the correlation line. Although the parameters used are only approximate and need to be refined, the

the asymmetry parameter A, in any case, will be appreciably greater than 0.04. Thus 0.04 represents the approximate limit of the asymmetry parameter, A, below which quadrupole splitting will not be observed in compounds where the contribution from the asymmetry in the ligand charge distribution is insignificant. Though no explanation can be offered for this surprising result, this confirms and quantifies the qualitative observation of Parish and Platt[4] that large difference in polarities of R-Sn and Sn-X bond is necessary for quadrupole splittings since larger the difference in the bond polarities, larger will be the asymmetry parameter, A. Parish and Platt suggested[4] that (i) the magnitude of the quadrupole splitting is governed primarily by the imbalence in the polarities of the tin-ligand σ-bonds, (ii) this effect may, in some cases, be supplemented by structural effects and (iii) π-bonding is a secondary factor. The correlation between the asymmetry parameter A and the experimental quadrupole splitting is in essential agreement with these suggestions.

The electrons which might be contributed to the vacant 5d orbital of the tin atom by the ligand through $d_\pi - p_\pi$ bonding are completely neglected in the present study. This was done in view of the fact that many important properties of organotin compounds can be satisfactorily interpreted even without invoking $d_\pi - p_\pi$ bonding[21,24-29]. The excellent correlations between the Mossbauer parameters and the calculated quantities further support this view.

Our conclusion, based on the present calculations and the foregoing discussion are (i) that the Mossbauer isomer shifts in

tetravalent organotin compounds can be interpreted by the calculated electron density at the tin nucleus, (ii) that the magnitude of quadrupole splitting is primarily determined by the asymmetry in the p-electron distribution at the tin atom and (iii) that, in a majority of cases, the asymmetry in charge distributions of the ligands exerts only minor effect on the electric field gradient.

Summary:

A method for calculating the electron density at the nucleus of tin atom in a tetravalent tin compound has been developed using the quantities available from Del Re calculations in conjunction with the formula given by Lees and Flinn. The calculated electron densities show a fair correlation with the experimental Mossbauer isomer shifts and a value of 3.2×10^{-4} is obtained for $\Delta R/R$ from the slope of the correlation line. This is in excellent agreement with the value of 3.3×10^{-4} determined by an independent method using internal electron conversion measurements. Further, an asymmetry parameter, A, which is a measure of the deviation of the p-electron distribution from the hypothetical spherically symmetric distribution in which the p-electrons would be distributed equally between the three p-orbitals has been defined and a method for its calculation has been developed. The experimental quadrupole splittings have been correlated and interpreted using this asymmetry parameter. The observed quadrupole splittings for a number of organotin compounds of the type R_nSnX_{4-n} when plotted against the calculated values of A, fall on two different correlation lines, almost parallel to each other. For compounds having $X = C_6F_5$ or C_6Cl_5 the asymmetry in the ligand charge distribution contributes appreciably to the observed quadrupole splitting

as indicated by the large intercept of the correlation line. When X = OF_3 or Cl, the correlation line meets the axis representing the asymmetry parameter at about 0.04, suggesting a very small contribution from the asymmetry in the ligand charge distribution. Interestingly, all compounds of the type R_nSnX_{4-n} (R = alkyl, Ph, Vi and X = Vi, Ph or p-substituted phenyl group) for which A is less than 0.04 do not show any quadrupole splitting.

The results indicate that (i) the Mossbauer isomer shifts in tetravalent organotin compounds can be interpreted in terms of the calculated electron density at the tin nucleus, (ii) the magnitude of quadrupole splitting is primarily determined by the asymmetry in the p-electron distribution at the tin atom, and (iii) in a majority of cases, the asymmetry in the charge distributions of the ligands exerts only a minor effect on the electrical field gradient.

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