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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD
I. HEATS OF ATOMISATION OF ORGANOTIN COMPOUNDS

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SUMMARY

A method for calculating heats of atomisation of organotin compounds by the Del Re approximation together with the Hückel procedure (where π-system is also present) has been developed. Results for thirteen compounds show an excellent correlation with the experimental heats of atomisation; deviation of the experimental values from the correlation curve is less than one percent.

INTRODUCTION

Although a great deal of attention has been recently paid to the interpretation of the properties of organosilicon compounds by quantum mechanical calculations[1-7], no similar systematic investigation of organotin compounds has yet been reported. In view of this we have carried out a systematic study of organotin compounds by approximate quantum mechanical methods. The main objective of the present work is to interpret and correlate many of the important properties such as heats of atomisation, bond lengths, NMR spectra, IR spectra and dipole moments of organotin compounds. In the present communication the method for calculating the heats of atomisation of organotin compounds by using Del Re's[8] approximation is developed. The correlation between the observed heats of atomisation and the calculated values is very striking and clearly demonstrates the usefulness of Del Re's method in calculating heats of atomisation of organotin compounds.

PROCEDURE

(A). *Calculation of σ-bond energies*

According to Del Re's approximation the energies of the σ-molecular orbitals between the two bonded atoms μ and ν are the solutions of the secular equation:

$$\begin{vmatrix} \alpha_0+\delta_\mu\cdot\beta-E & \varepsilon_{\mu\nu}\cdot\beta \\ \varepsilon_{\mu\nu}\cdot\beta & \alpha_0+\delta_\nu\cdot\beta-E \end{vmatrix} = 0 \qquad (1)$$

Eqn. (1) readily gives the energy of the bonding orbitals, E, as:

$$E = \alpha_0 + [\delta_\mu + \delta_\nu + \sqrt{4\varepsilon_{\mu\nu}^2 + (\delta_\mu - \delta_\nu)^2}] \cdot \beta/2 \tag{2}$$

The total energy of the two electrons occupying the bond is:

$$2\alpha_0 + [\delta_\mu + \delta_\nu + \sqrt{4\varepsilon_{\mu\nu}^2 + (\delta_\mu - \delta_\nu)^2}] \cdot \beta$$

Hence the bond energy, $E_{\mu\nu}$, which is equivalent to the net stabilization, is given by:

$$E_{\mu\nu} = [(\delta_\mu + \delta_\nu) + \sqrt{4\varepsilon_{\mu\nu}^2 + (\delta_\mu - \delta_\nu)^2} - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{3}$$

The total σ-bond energy, E_σ, is given by:

$$E_\sigma = \sum_{\text{all bonds}} E_{\mu\nu} \tag{4}$$

Since the quantities δ_μ and δ_ν may be easily calculated by Del Re's method provided all the necessary Del Re parameters are known, the total bond energy of the σ frame work may be computed in terms of the standard Del Re resonance parameter, β, by using eqns. (3) and (4).

(*B*). *Calculation of the π-bond energies*

In compounds such as tetraphenyltin, trimethylvinyltin etc., in which a π-system is present, it is necessary to obtain the π-bond energy in addition to the σ-bond energy. The π-bond energy may be calculated by the standard Hückel procedure. However, the replacement of a C–H bond of the parent hydrocarbon by C–Sn bond in the organotin compound will primarily alter the Coulomb integral, α, of the attached carbon atom. By writing this integral as:

$$\alpha = \alpha_0 + h \cdot \beta_\pi \tag{5}$$

where α_0 is the Coulomb integral for all the carbon atoms except that bonded to tin and β_π is the resonance integral for the $(C_p–C_p)\pi$ bond, the total π-energy may be readily calculated provided the value of h is known. Nagy *et al.*[6] in their recent treatment of organosilicon compounds have treated this as a variable parameter. However, in a general treatment of a whole group of compounds, it is desirable to have a logical procedure for evaluating h. In the Hückel LCAO MO procedure the magnitude of h for a hetero-atom is generally taken as the difference in the Pauling electronegativities of the heteroatom and carbon. Therefore a consistent procedure for evaluating the parameter "h" for a substituted carbon atom appears to be calculation of the change in its electronegativity with respect to the other carbon atoms.

According to the Allred–Rochow equation[9], the Pauling electronegativity, x is given by the relation:

$$x = 0.359\, Z_{\text{eff}}/r^2 + 0.744 \tag{6}$$

Where Z_{eff} is the effective charge acting on an imaginary outer electron and r, its covalent radius. For a normal carbon atom, Z_{eff} and r are 2.90 and 0.77 Å respectively. The presence of a partial charge on the carbon atom will, however, cause a change in the Z_{eff}. Using Slater's procedure[10] Z'_{eff}, the effective charge for a carbon atom having a partial charge δq is given by:

$$Z'_{eff} = Z_{eff} + 0.35\,\delta q \tag{7}$$

Therefore the change in the electronegativity of the carbon atom bonded to a tin atom relative to that to a hydrogen atom will be given by:

$$\begin{aligned} h = \Delta x &= 0.359 \times 0.35\,(\delta q - \delta^0 q)/r^2 \\ &= 0.21\,(\delta q - \delta^0 q) \end{aligned} \tag{8}$$

where $\delta^0 q$ and δq are the partial charges on a carbon atom in the parent hydrocarbon (where the carbon atom coulomb integrals are assigned the standard value α^0) and in the organotin compound, respectively. Since the charges on all the carbon atoms are different from those in the parent hydrocarbon, all the carbon atoms should strictly be assigned a different Coulomb integral in the tin compound, but, this difference is negligible for all carbon atoms except that directly bonded to the metal. Incidentally, this provides a justification for the frequently adopted procedure of assigning the standard value α^0 to all carbon atoms except that at which substitution has taken place. In the present calculations no corrections in the Coulomb integrals of all the carbon atoms has been considered in view of their negligible contribution to the calculated energy.

As $\delta^0 q$ and δq may be calculated by Del Re's procedure it is now possible to calculate the parameter h. For the vinyl and the phenyl groups $\delta^0 q$ are found to be 0.109 and 0.053 by Del Re calculations on ethylene and benzene respectively.

As h is found to be rather small for all the compounds discussed here, the π-energy may be obtained with very good accuracy by a perturbation treatment[11], which gives:

$$E_\pi = E_\pi^0 + q_r \cdot \delta\alpha_r + \tfrac{1}{2}\pi_{r,r} \cdot (\delta\alpha_r)^2 \tag{9}$$

where E_π^0 is the energy of the parent hydrocarbon, q_r and $\pi_{r,r}$ are the electron density and atom–atom polarizabilities and $\delta\alpha_r$ is the change in the coulomb integral of the r-th atom. By using the tabulated values of q_r, π_r and E_π for benzene[11], together with eqn. (5), eqn. (9) takes the following form for the phenyl groups:

$$E_\pi = 8\,\beta_\pi + h \cdot \beta_\pi + 0.2 \cdot h^2 \cdot \beta_\pi \tag{10}$$

where E_π is the π-energy of a phenyl group in the organotin compound. For the vinyl group, the π-energy has been calculated directly by solving the appropriate 2×2 secular equation. As the π-energy is obtained in terms of the Hückel resonance integral, β_π, appropriate to the π-bond, it is necessary to calculate the ratio β_π/β, in order that the calculated energy may be correlated with the total bond energy of the molecule, *i.e.*, its heat of atomisation. An approximate method for evaluating this ratio will be to use the well known Lennard–Jones' method[12], frequently applied to π-system. According to Lennard–Jones' argument, the ratio in the present case will be given by:

$$\beta_\pi/\beta = (E_{C=C} - E_{C-C})/E_{C-C} \tag{11}$$

where $E_{C=C}$ and E_{C-C} are the energies of carbon–carbon double bond and single bond, respectively. As the C–C distance in compounds having a double bond is considerably different from that in a pure single bond, the energy appropriate to the eqn. (11) is not the observed single bond energy, but one which corresponds to a hypothetical carbon–carbon single bond having a bond length of approximately 1.35 Å. Although this quantity is not directly available by experiment, it may be evaluated by assuming that the energy of a carbon–carbon single bond of a given length is proportional to the corresponding overlap. With this assumption, E_{C-C} is given by the equation:

$$E_{C-C} = S_1 \cdot E'_{C-C}/S_2 \tag{12}$$

where E'_{C-C} is the standard carbon–carbon single bond energy, S_1 and S_2 are the σ-overlaps between two $C\text{-}sp^2$ orbitals at a distance of 1.35 Å and two $C\text{-}sp^3$ orbitals at a distance 1.54 Å respectively. Taking the standard values of $E_{C=C}$ and E_{C-C} as 148.4 and 83.6 kcal/mole respectively[13], and S_1 and S_2 as 0.76 and 0.65 respectively[14], a value of 0.52 is obtained for β_π/β. The π-energy may therefore be calculated in terms of the standard Del Re resonance integral, β, by multiplying the calculated π-energy, E_π by 0.52. The total bond energy of the system is thus obtained by adding the σ and π contributions.

Although the possibility of d_π–p_π bonding between tin and carbon atom can not be ruled out, this effect has not been considered here. The main reasons for neglecting d_π–p_π interaction are as follows: (*a*) the large energy difference between tin d_π and carbon p_π orbitals, coupled with small overlap precludes significant contribution of such bonding to the total energy, and (*b*) the possibility of correlating such properties like NMR, IR and dipole moments of organotin compounds without invoking d_π–p_π bonding. This aspect is discussed below.

(*C*). *Evaluation of Del Re parameters*

The Del Re parameters for Sn–C and Sn–Cl bonds have been determined from the dipole moments of Me_3SnCl, Me_2SnCl_2 and $MeSnCl_3$ together with the bond energies of the Sn–C and Sn–Cl bonds. The δ^0 value for the tin atom is based on its electronegativity. For all other bonds the parameters given by Del Re has been used. Recently Nagy *et al.*[2] have modified the inductive parameters for the C–H bond, but the observed partial bond moment of the C–H bond is more consistent with the original set given by Del Re, and furthermore the calculated charges on the hydrogen

TABLE 1

Del Re PARAMETERS

Bond	$\nu_{A(B)}$	$\nu_{B(A)}$	ε_{AB}	δ^0_A	δ^0_B
C–H	0.30	0.40	1.00	0.07 (sp^3) 0.12 (sp^2)	0.00
C–C	0.10	0.10	1.00	0.07 (sp^3) 0.12 (sp^2)	0.07 (sp^3) 0.12 (sp^2)
Sn–C	0.10	0.10	0.50	−0.10	0.07 (sp^3) 0.12 (sp^2)
Sn–Cl	0.20	0.40	0.45	−0.10	0.35

atoms are closer to the values obtained by the well known σ-molecular orbital theory of Fukui[15]. The results of our present investigation also indicates that the original set of parameters is the more consistent, at least in the case of organotin compounds. The Del Re parameters are given in Table 1.

RESULTS

The calculated σ and π bond energies for thirteen organotin compounds are given in Table 2. These energies are in terms of the standard Del Re resonance integral, β. Included in the same table are the experimental heats of atomisation, taken from Skinner[16]. For the compounds Me_3SnCl, Et_3SnCl and $EtSnCl_3$ the heats of atomisation have been calculated from the reported values of their heats of formation in the liquid state, $\Delta H^{25°}(L)$[17], by computing the heats of vapourisation, ΔH_v, from Trouton's rule and the Wheland equation[18]. Fig. 1 shows the correlation between the calculated and observed energies. The correlation is excellent and the least square line for the thirteen points is given by:

$$\Delta H = 44.06\,x + 92.7 \tag{13}$$

where ΔH is the heat of atomisation in kcal/mole and x is the calculated energy in units of β.

The degree of accuracy with which the present calculations correlate the experimental heats of atomisation can be readily understood by comparing the observed values with those calculated from eqn. (13), which are also included in Table 2. The percentage deviation is within one percent for all the compounds except ethyltin trichloride, for which the heat of atomisation was computed from its provisional heat of formation reported by Skinner[17]. In view of the very approximate nature of the Del Re method such an excellent correlation is surprising. Equally surprising is the presence of a constant term equal to 92.7 kcal/mole in the correlation curve. Similar

TABLE 2

CALCULATED AND EXPERIMENTAL HEATS OF ATOMISATION OF ORGANOTIN COMPOUNDS

Compound	$E_{\sigma/\beta}$	$E_{\pi/\beta}$	Total, in units of β	Cald. heat of atomisation (kcal/mole)	Exper. heat of atomisation (kcal/mole)	deviation (%)
Me_4Sn	29.18	0	29.18	1378.4	1385.4	−0.5
Et_4Sn	54.52	0	54.52	2494.9	2491.9	0.1
Pr_4Sn	79.81	0	79.81	3609.2	3616.2	−0.2
Bu_4Sn	105.10	0	105.10	4723.5	4734.9	−0.2
Me_3EtSn	35.57	0	35.57	1659.9	1663.0	−0.2
Me_3PhSn	46.61	4.15	50.76	2329.2	2314.5	0.6
$Me_3BenzSn$	52.44	4.16	56.60	2586.6	2595.5	−0.3
Me_3ViSn	31.45	1.03	32.48	1524.2	1530.7	−0.4
Ph_4Sn	97.43	16.59	114.02	5116.5	5101.3	0.3
Me_2SnCl_2	17.38	0	17.38	858.5	853.6	0.6
Me_3SnCl	23.28	0	23.28	1118.4	1124.6	−0.6
$EtSnCl_3$	17.79	0	17.79	876.5	863.3	1.5
Et_3SnCl	42.28	0	42.28	1955.6	1956.0	0.0

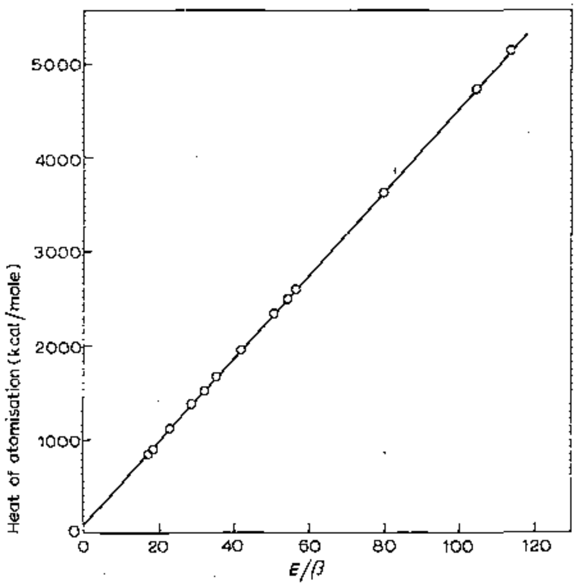

Fig. 1. Plot of the heats of atomisations of some organotin compounds *vs.* the total bond energy (calcd.) in units of β.

behaviour is shown by Hückel energy for π-transitions when plotted against the observed transition energies[19]. The calculations indicate a close similarity between the results of Hückel π-MO and Del Re σ-orbital treatment in their respective fields.

Another interesting point to emerge from the present calculations concerns the value of β_π. Since the value of β is found to be 44.06 kcal/mole and β_π/β has been shown to be 0.52, β_π is calculated to be 22.9 kcal/mole. This value is very close to 20 kcal/mole obtained from Hückel MO calculations for the resonance energies of aromatic hydrocarbons[20]. This provides strong support to the validity of the arguments used for the computation of π-energy.

The present calculations indicate that the Del Re method provides a very simple, yet reliable, method for the interpretation and correlation of the properties of organometallic compounds.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD
II. DIPOLE MOMENTS OF ORGANOTIN COMPOUNDS AND VARIATION IN THE TIN–CHLORINE AND TIN–CARBON BOND POLARITY

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SUMMARY

The electric dipole moments of 20 organotin compounds containing methyl, ethyl, tert-butyl, n-butyl, phenyl and vinyl groups have been calculated using an approximate quantum mechanical procedure. The σ-charge distributions have been calculated using the Del Re method and the π-charges by the Hückel LCAO MO method using the perturbation technique. Agreement with the experimental values is generally good. The calculated bond polarity of the tin–chlorine bond decreases in the order $R_3SnCl > R_2SnCl_2 > RSnCl_3 > SnCl_4$ in accordance with the variation in the nuclear quadrupole coupling constant of chlorine in these molecules. The tin–carbon bond polarity in R_nSnCl_{4-n} type compounds follow the order vinyl > phenyl > methyl > ethyl > n-butyl > tert-butyl as would be expected from the relative electronegativities of the R groups.

In the previous communication[1] it was shown that the heat of atomisation of organotin compounds may be calculated with remarkable accuracy by the Del Re method. As a further test for the applicability of the Del Re method we have used the theoretical σ-charge distributions obtained by this procedure to calculate the electric dipole moments of the organotin compounds. The agreement with the experimental values is remarkably good.

PROCEDURE

Calculation of σ-moments

In the present calculations the σ-charge distributions have been calculated by using the Del Re parameters given in our previous communication[1]. The Del Re parameters for the Sn–H bond, given in Table 1, have been determined from the dipole

TABLE 1

DEL RE PARAMETERS

Bond	$\nu_{A(B)}$	$\nu_{B(A)}$	ε_{AB}	δ_{A^0}	δ_{B^0}
Sn–H	0.50	−0.40	0.40	−0.10	0.00

moment of CH_3SnH_3 along with NMR and IR data for organotin hydrides. In our calculation the lengths of Sn–C, C–C, C=C (vinyl), C=C (phenyl), C–H, Sn–Cl and Sn–H bonds are taken to be 2.18 Å, 1.54 Å, 1.35 Å, 1.40 Å, 1.09 Å, 2.37 Å, and 1.70 Å, respectively[2-4], for all the compounds except methyltin chlorides, for which the electron diffraction data[2] have been used. For the tin atom a tetrahedral geometry has been assumed which is consistent with the X-ray and electron diffraction data[2,5,6] where these are available. In the ethyl- and vinyltin compounds, when more than one geometry is possible, the sterically most favoured one has been assumed in the dipole moment calculation. However, the dipole moments of the various configurations are found to differ by less than ±0.06 D, which is much less than the variation in the reported data.

B. Calculation of π-moments

In the phenyl- and vinyltin compounds it is necessary to calculate the contribution of the π-charge distribution to the dipole moment. In Part I we showed that in the organotin compounds the Coulomb integral of the carbon atom attached to the tin atom is primarily altered, and a general method for calculating the Coulomb integral of this carbon atom was developed[1]. Since the Coulomb parameter "h" for the attached carbon atom has been found to be rather small for all the compounds discussed here, the π-charges may be obtained with very good accuracy by the perturbation technique[7] which gives

$$\Delta q_s = \pi_{s,r} \cdot \Delta\alpha_r$$

where Δq_s is the change in the π-charge at the s^{th} atom due to a change in the Coulomb integral at the r^{th} atom by an amount $\Delta\alpha_r$, and $\pi_{s,r}$ is the atom–atom polarizability, values which have been taken from Coulson and Streitwieser[7]. However, in the case of vinyl compounds the π-charges at the carbon atoms have been calculated directly by solving the appropriate 2 × 2 secular equation.

RESULTS

The calculated values of the dipole moments of a number of organotin compounds along with the experimental dipole moments are given in Table 2. Allowing for the large variations in the reported dipole moments the agreement between the calculated and the observed values is generally very good.

A very significant feature of the present calculation is the change in the Sn–Cl bond polarity in going from Me_3SnCl to $SnCl_4$. In order to account for the variations in the dipole moment in the series R_3SnCl, R_2SnCl_2, and $RSnCl_3$, Lorberth and Noth[8] and Huang *et al.*[9] have argued in favour of increase in the Sn–Cl bond polarity with progressive chlorine substitution, although the nuclear quadrupole coupling constants of organotin chlorides[10] indicate a reverse order of the Sn–Cl bond polarity. These apparently contradictory conclusions have been reconciled in our calculations. An examination of the variation in the bond polarities of the various bonds of methyltin chlorides given in Table 3 shows that the Sn–Cl bond polarity decreases from Me_3SnCl to $MeSnCl_3$ as would be expected from the nuclear quadrupole coupling constant data. However, the Sn–C bond polarity also decreases concurrently and, indeed, is reversed in $MeSnCl_3$. Thus, although the Sn–Cl bond moment decreases in the series,

TABLE 2

CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS OF ORGANOTIN COMPOUNDS IN DEBYE UNITS

Compound	Dipole moment		Refs.
	Calcd.	Found	
Me_3SnCl	3.46	3.46–3.52	8, 9, 13
Me_2SnCl_2	4.04	4.14–4.21	8, 9, 13
$MeSnCl_3$	3.63	3.62–3.77	8, 13
Et_3SnCl	3.55	3.44–3.80	9, 14, 15
Et_2SnCl_2	4.14	3.85–4.47	9, 14, 15
$EtSnCl_3$	3.73	4.08	8
Me_3SnH	0.67		
Me_2SnH_2	0.78		
$MeSnH_3$	0.65	0.68	16
Me_3PhSn	0.54	0.51	17
Et_3PhSn	0.50	0.50	18
$EtPh_3Sn$	0.51	0.73	18
Me_3ViSn	0.52	0.45	19
t-Bu_2SnCl_2	4.14	4.34	9
Vi_3SnCl	3.05	3.00	9
Vi_2SnCl_2	3.65	4.06	9
$ViSnCl_3$	3.34	3.77	9
Ph_3SnCl	3.01	3.30–3.46	8, 9, 12, 14
Ph_2SnCl_2	3.64	3.59–4.31	8, 9, 12
$PhSnCl_3$	3.39	3.99–4.30	8, 9, 12

TABLE 3

POLARITY (PERCENT) OF DIFFERENT BONDS IN METHYLTIN CHLORIDES

Compound	Sn–Cl	Sn–C	H–C
Me_3SnCl	38.68	10.66	3.30
Me_2SnCl_2	33.79	4.48	3.64
$MeSnCl_3$	28.07	-2.77^a	4.05

[a] Negative sign indicates reversal of polarity.

TABLE 4

COMPARISON OF CHARGE ON THE CHLORINE ATOM WITH ITS NUCLEAR QUADRUPOLE COUPLING CONSTANT

Compound	Charge on Cl	Coupling const. (MHz)
Bu_2SnCl_2	−0.338	34.6
$BuSnCl_3$	−0.281	43.2
$SnCl_4$	−0.212	48.2

the decrease in the Sn–C bond moment, which acts in the opposite direction, leads to an overall higher dipole moment.

That the calculated bond polarities are essentially correct is also indicated by the data given in Table 4, in which nuclear quadrupole coupling constants of chlorine in Bu_2SnCl_2, $BuSnCl_3$ and $SnCl_4$ are compared with the calculated charge on the chlorine atom.

A feature which strongly indicates the validity of the Del Re calculations in the study of organotin compounds is the calculated variation in the Sn–C bond polarity in R_nSnCl_{4-n} compounds. Because the electronegativity sequence is phenyl > methyl > ethyl > n-butyl > tert-butyl, it is expected that the Sn–C bond polarity would follow the same order. This is clearly demonstrated by the data given in Table 5.

TABLE 5

VARIATION IN THE TIN–CARBON BOND POLARITY (PERCENT) OF R_nSnCl_{4-n} COMPOUNDS

R	R_3SnCl	R_2SnCl_2	$RSnCl_3$[a]
Vi	13.97	7.95	0.82
Ph	13.82	7.70	0.45
Me	10.66	4.48	−2.77
Et	10.61	4.29	−3.14
Bu	10.58	4.25	−3.19
t-Bu	10.55	4.05	−3.64

[a] Negative sign indicates reversal of polarity.

The Sn–C bond polarities in vinyltin compounds indicates the vinyl group is more electronegative than the phenyl group, which is consistent with the results of cleavage of symmetrical organomercury compounds by HCl[11].

Although the present calculations account for the dipole moments as well as the variation in the bond polarities satisfactorily, in two cases, namely, $PhSnCl_3$ and $ViSnCl_3$, the calculated moments are somewhat low. The high dipole moment of these compounds have been attributed to d_π–p_π bonding between tin and carbon by Huang *et al.*[9]. However, the dipole moments of organotin chlorides, particularly those of R_2SnCl_2 and $RSnCl_3$ type compounds, show a strong solvent dependence. For example, the dipole moment of $PhSnCl_3$ varies from 3.99 to 5.81 D depending on the solvent[12], indicating a strong solvent–solute interaction in this case. Because of such large interactions it is not possible to obtain the dipole moment of the free molecule to which our calculation applies. In any case, the dipole moment of phenyltin trichloride in the absence of any interaction would be certainly lower than 3.99 D, which is the value in hexane, since the observed dipole moment increases in solvents like dioxane for which the interaction with the solvent is expected to be greater. It may be noted that comparatively large deviations from the calculated values occur only in such cases. Thus, it appears that the discrepancy between the calculated and the observed dipole moments in such cases is more likely to be due to error in the experimental values rather than to d_π–p_π bonding. This view is supported by the fact that our calculations satisfactorily account for such diverse properties as heat of atomisation, bond polarities and nuclear quadrupole coupling constants without the need to invoke d_π–p_π bonding. Further, it will be shown in the subsequent papers that even the chemical shifts, tin–chlorine stretching frequencies, and tin–chlorine distances in organotin chlorides can be accounted for without invoking d_π–p_π bonding.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD
III. VARIATIONS IN TIN–CHLORINE, TIN–CARBON AND TIN-HYDROGEN STRETCHING FREQUENCIES AND TIN–CHLORINE BOND DISTANCE IN ORGANOTIN COMPOUNDS

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SUMMARY

The concept of bond order has been extended to Del Re calculations, and the bond orders of tin–chlorine and tin–carbon bonds in $Me_{4-n}SnCl_n$ ($n=1$ to 4) type compounds have been calculated. The tin–chlorine bond order increases progressively from 0.922 in Me_3SnCl to 0.977 in $SnCl_4$, and correlates satisfactorily with the experimental tin–chlorine bond distances. The tin–carbon bond order, on the other hand, remains almost constant, in agreement with the constancy of tin–carbon bond distance in the series. The average tin–chlorine, tin–carbon and tin–hydrogen stretching frequencies in similar compounds vary linearly with the calculated bond polarities indicating variation in bond polarity to be the dominating factor. The unusually low values of the tin–carbon stretching frequency for the tin–vinyl bond compared to the tin–methyl bond in Me_3ViSn and Et_2Vi_2Sn can also be explained in terms of larger polarity of the tin–vinyl bond in these compounds.

INTRODUCTION

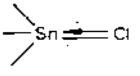
In our previous communications[1,2] we have shown that the Del Re method in conjunction with Huckel LCAO MO method can account for the heats of atomisation and dipole moments of organotin compounds with striking accuracy. In the present communication the concept of bond order has been extended to Del Re calculations to define partial bond orders between pairs of atomic orbitals. The calculated bond orders have been correlated with the observed tin–chlorine bond distances in organotin chlorides. Similarly the variations in the stretching frequencies of tin–chlorine, tin–carbon and tin–hydrogen bonds have been correlated with the bond polarity.

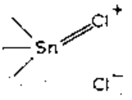
RESULTS AND DISCUSSION

(1). *Variation in the tin–chlorine bond distance in methyltin halides*

Electron diffraction measurements on methyltin halides by Skinner *et al.*[3]

have shown that the tin–chlorine bond distance decreases gradually from 2.37 Å in trimethyltin chloride to 2.30 Å in tin tetrachloride. According to Skinner *et al.*[3], there may be various reasons for the observed shortening of the tin–chlorine bond distance with increase in the number of tin–chlorine bonds in organotin chlorides,


(I)


(II)

viz., (*i*) increased contribution from structure (I) involving multiple bond between tin and chlorine, or (*ii*) importance of the ionic structure (II). But the more plausible explanation given by them is the increase of the positive charge on the tin atom with progressive chlorine substitution and a corresponding decrease of normal radius of the tin atom accompanied by decreased elongation of the halogen atom due to reduced bond polarity of the tin–chlorine bond and a greater attraction of the central atom for the halogen atom. This view is strongly supported by the calculated charge distributions in methyltin chlorides given in Fig. 1. The results show the expected increase in the positive charge on the tin atom with progressive chlorine substitution.

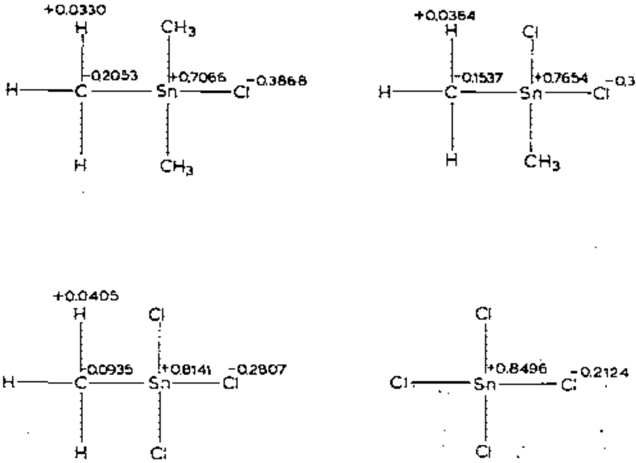


Fig. 1. Charge distributions in $Me_{4-n}Cl_n$ compounds. (a) Me_3SnCl; (b) Me_2SnCl_2; (c) $MeSnCl_3$; (d) $SnCl_4$.

On the other hand, the tin–chlorine bond polarity decreases gradually from 38.68 % in trimethyltin chloride to 21.24 % in tin tetrachloride. Although the shortening of tin–chlorine distance in organotin halides can be qualitatively accounted for by the calculated charge distributions, it is, however, more useful to define and evaluate parameters with which the bond distances may be quantitatively correlated. In the π-electron calculations the bond order has been found to be the most important quantity in this respect. Although the Del Re orbitals differ from the π-orbitals in being strictly localized between the two bonded atoms, the concept of bond order can nevertheless be extended to give a partial bond order between the pair of atomic orbitals forming the bond. Thus, if the bonding orbital ψ corresponding to the atoms μ and ν is written as:

$$\psi = c_\mu \cdot \psi_\mu + c_\nu \cdot \psi_\nu \tag{1}$$

the corresponding bond order, $p_{\mu\nu}$ will be given by:

$$p_{\mu\nu} = 2c_\mu \cdot c_\nu \tag{2}$$

However, it is more convenient to express the bond order in terms of bond charges $Q_{\mu\nu}$ which are normally evaluated in all Del Re calculations rather than the actual orbitals which are not clearly defined in Del Re procedure. By using the relations:

$$c_\mu^2 + c_\nu^2 = 1 \tag{3}$$

and

$$c_\nu^2 - c_\mu^2 = Q_{\mu\nu} \tag{4}$$

it may be easily shown that:

$$p_{\mu\nu} = (1 - Q_{\mu\nu}^2)^{\frac{1}{2}} \tag{5}$$

The tin–chlorine bond orders in methyltin chlorides, calculated from eqn. (5) using the Del Re parameters given in the previous communications, are given in Table 1 along with the experimental tin–chlorine bond distances. In view of the

TABLE 1

BOND ORDER OF TIN–CHLORINE BONDS AND TIN–CHLORINE BOND DISTANCES IN METHYLTIN CHLORIDES

Compound	Bond order	Bond distance (Å)
Me_3SnCl	0.922	2.37
Me_2SnCl_2	0.941	2.34
$MeSnCl_3$	0.960	2.32
$SnCl_4$	0.977	2.30

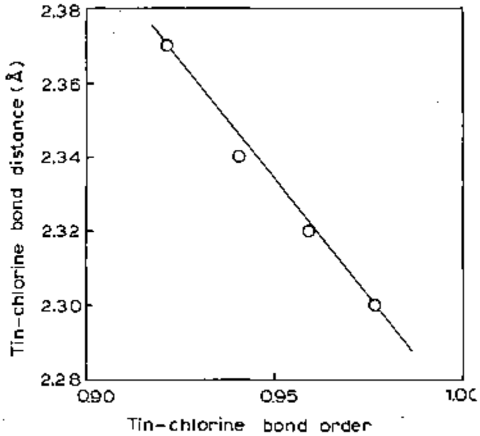


Fig. 2. Correlation between tin–chlorine bond order and tin–chlorine bond distance.

excellent correlation between the calculated bond orders and the experimental bond lengths shown in Fig. 2, we feel that the gradual shortening of tin chlorine distance with progressive chlorine substitution is primarily due to changes in the tin–chlorine bond order rather than due to any d_π–p_π bonding between tin and chlorine.

It is also gratifying to note that the tin-carbon bond order turns out to be almost constant in methyltin halides (0.994 in Me_3SnCl, 0.999 in both Me_2SnCl_2 and $MeSnCl_3$) in full agreement with the constancy of tin–carbon distance in these compounds[3].

(2). *Variation in tin chlorine, tin–carbon and tin–hydrogen stretching frequencies*

Like tin–chlorine bond distance, the tin–chlorine stretching frequencies also show a regular variation in the series $Me_{4-n}SnCl_n$ ($n = 1, 2, 3$ and 4). The average tin chlorine stretching frequencies (weighted with respect to degeneracy) are 331 ($n = 1$), 344 ($n = 2$), 367 ($n = 3$) and 394 cm^{-1} ($n = 4$)[4]. Similarly, the average tin–carbon stretching frequency in the series increases from 524 cm^{-1} in tetramethyltin to 550 cm^{-1} in methyltin trichloride[5,6]. The gradual increase in the average stretching frequencies of both tin–chlorine and tin–carbon bonds in these geometrically similar molecules

TABLE 2

POLARITIES, P, OF TIN–CHLORINE AND TIN–CARBON BONDS AND AVERAGE STRETCHING FREQUENCIES IN $Me_{4-n}SnCl_n$ COMPOUNDS

Compound	P(Sn–Cl) (%)	ν(Sn–Cl)[a] (cm^{-1})	P(Sn–C) (%)	ν(Sn–C)[a] (cm^{-1})
Me_4Sn			16.00	524
Me_3SnCl	38.68	331	10.66	534
Me_2SnCl_2	33.79	344	4.48	544
$MeSnCl_3$	28.07	367	2.77	550
$SnCl_4$	21.24	394		

[a] Average weighted with respect to degeneracy.

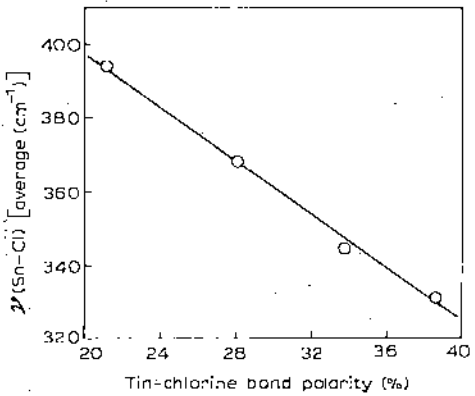


Fig. 3. Correlation between tin–chlorine bond polarity and tin–chlorine stretching frequency.

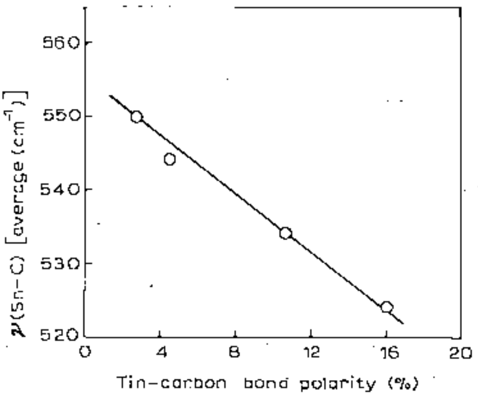


Fig. 4. Correlation between tin–carbon bond polarity and tin–carbon stretching frequency.

(all members of the series $Me_{4-n}SnCl_n$, $n=0$ to 4, are tetrahedral[3,7]) must be attributed to (*i*) a concurrent increase of d_π–p_π contributions in both tin–carbon and tin–chlorine bonds, or (*ii*) a gradual decrease in the bond polarity. In order to see whether the changes in the bond polarity can account for the observed variations in the stretching frequencies the bond polarities of the tin–chlorine and tin–carbon bonds in the series $Me_{4-n}SnCl_n$ ($n=0$ to 4) have been calculated by the usual Del Re procedure using the parameters previously given[1,2]. These data are given in Table 2. The weighted average frequencies listed in Table 2 have been calculated from the reported IR and Raman data[4–6], care being taken to select data measured under identical conditions as far as possible. Figs. 3 and 4 show that the average stretching frequencies vary linearly with the bond polarities as would be expected if the bond polarity alone was the dominating factor for the observed variations in vibrational frequencies. This conclusion is further supported by the fact that ν[Sn–C(vinyl)] in Me_3ViSn and Et_2Vi_2Sn are markedly lower than ν[Sn–C(methyl)][8] though the tin–vinyl bond would be expected to be stiffer compared to the tin–methyl bond if d_π–p_π bonding was operative due to the availability of a favourably disposed p_π orbital at the vinyl carbon and also due to increase in the positive charge on the tin atom. Del Re calculations, however, show that the tin–carbon(vinyl) bond polarities are 20.51 and 20.04 % in Me_3ViSn and Et_2Vi_2Sn respectively compared to 16.00 % for the tin–carbon bond in Me_4Sn. Thus, the observed[8] frequencies, *viz.* 462 and 469 cm^{-1}, are in full agreement with the calculated bond polarities. It must be pointed out that such linear correlation between bond polarity and stretching frequency may be obtained only within a group of closely similar compounds since the vibrational frequencies, even if averaged with respect to degeneracy, are often very sensitive to changes in the

TABLE 3

POLARITY AND STRETCHING FREQUENCIES OF TIN–HYDROGEN BOND IN n-BUTYLTIN HYDRIDES

Compound	Polarity (%)	ν(Sn–H) (cm^{-1})
Bu_3SnH	10.19	1808
Bu_2SnH_2	9.99	1842
$BuSnH_3$	9.84	1865

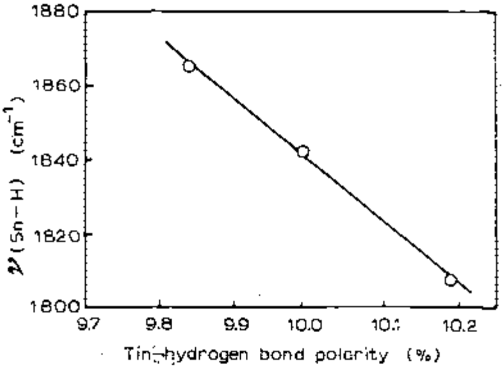


Fig. 5. Correlation between tin–hydrogen bond polarity and tin–hydrogen stretching frequencies.

geometry due to the possibility of coupling with other vibrational modes of the molecule. For example, the marked lowering of ν(Sn–C) with increasing chain length of the alkyl substituents in R_4Sn compounds can not be explained on the basis of bond polarities since the calculated tin–carbon bond polarities do not show appreciable variation.

Like tin–chlorine and tin–carbon frequencies, tin–hydrogen frequencies also show a linear variation with the tin–hydrogen bond polarity. The data are listed in Table 3 and the correlation is shown in Fig. 5. The *n*-butyl tin hydrides have been chosen since IR data under comparable conditions are available for this series[9].

In view of the present correlations and our previous calculations on heats of atomisation and dipole moments of organotin compounds it may be concluded that d_π-p_π bonding in organotin compounds, if any, is very insignificant, and that most of the important physical properties of organotin compounds may be explained satisfactorily without invoking d_π-p_π bonding.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

IV. NMR SPECTRA OF ORGANOTIN COMPOUNDS

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SUMMARY

Del Re calculations have been extended to correlate and interpret the NMR data in the organotin compounds. The methyl proton chemical shifts have been correlated with the partial charge on the methyl hydrogen atom. Variations in ^{13}C–H and tin–proton coupling constants have been correlated with the calculated Coulomb integral values, and the relationship has been interpreted in terms of the change in the *s*-character of the appropriate atomic orbital using isovalent hybridisation arguments in conjunction with the calculated theoretical quantities.

INTRODUCTION

NMR spectroscopy has been widely used in the study of organotin compounds. The volume of published data on proton chemical shifts, tin–proton spin–spin coupling constants and ^{13}C–H spin–spin coupling constants etc. in organotin compounds is considerable and comprehensive compilations are available[1–3]. Although there have been several discussions of the factors influencing chemical shifts[4–7], tin–proton spin–spin coupling constants[8–10] and ^{13}C–H spin–spin coupling constants[11,12], there has been no general correlation of these quantities with theoretically significant parameters, such as partial charges on the nucleus. We have therefore, attempted to systematize and correlate the various NMR data on organotin compounds in terms of partial charges and Coulomb integral parameters calculated by the Del Re method.

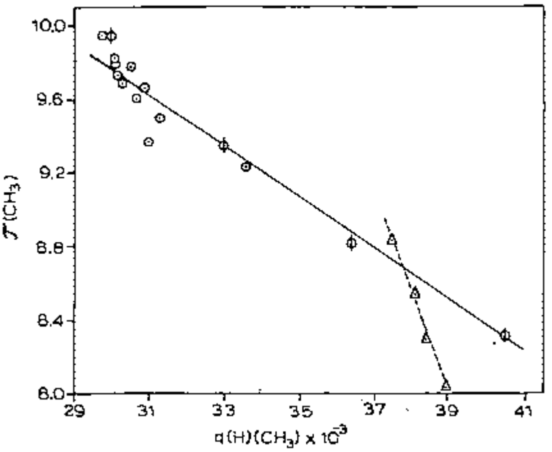
RESULTS AND DISCUSSIONS

(*A*). *Proton chemical shifts of organotin compounds*

It has been shown[13] that proton chemical shifts can be correlated with the electron density or the partial charge on the hydrogen atom provided the other factors influencing the chemical shifts, *viz*., neighbour anisotropy effects, ring current effects, etc., are either absent or remain constant within the group of compounds being studied.

Since unsaturated and aromatic groups are known to exert appreciable anisotropy and ring current effects, the present study is restricted to methyltin compounds only. The partial charges on the methyl protons calculated by using the previously reported Del Re parameters[14,15], are given in Table 1 along with the reported chemical shifts[1-3] [$\tau(CH_3)$] for a number of alkyltin compounds, and the correlation is shown in Fig. 1. In view of the large solvent dependence of the proton chemical shifts[4], and consequent uncertainty in $\tau(CH_3)$, the correlation is fairly good. It is interesting to note that values of $\tau(CH_3)$ in the ethyltin compounds are lower than would be expected from the straight line shown in Fig. 1. This is consistent with the conclusion by Drago and Matwiyoff[11,12] that large anisotropic contributions to the proton chemical shifts exist in the organotin compounds. Since the methyl protons in the ethyltin compounds are further removed from the tin atom than they are in the methyltin compounds, the shielding due to the anisotropic effect of the tin atom will be less in the ethyltin compounds, leading to lower $\tau(CH_3)$ values. This conclusion is further supported by the existence of another linear correlation between $\tau(CH_3)$ and q(H) for the ethyl series (shown by the dashed line in Fig. 1), since the anisotropic effect, although different from that in the methyl series, remains constant within the series because of the identical disposition of the methyl groups.

An interesting NMR parameter that has often been used in the study of the ethyl compounds is the difference in the chemical shifts between methyl and methylene protons [$\tau(CH_3)-\tau(CH_2)$], and an approximately linear correlation between $\Delta\tau$ and the electronegativity of the substituent X in the series C_2H_5X has been established[16-18]. Although the substituent atom, X, has been varied in all these studies, variations in $\Delta\tau$ will occur even when X remains the same, depending on the other groups attached to it, as is evident from the data given in Table 2. This is because the actual electronegativity of the substituent atom will depend on its environment, owing to the variations in the effective nuclear charge[14] (the Pauling or other electronegativities assigned to an element refer to some standard compound of the element). Since there is no established method for estimating such electronegativities, the Cou-



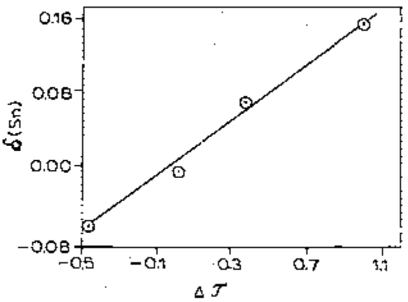


Fig. 1. Correlation between the partial charge q(H) and chemical shift of methyl hydrogen $\tau(CH_3)$ of some organotin compounds (⊙, methyltin compounds; △, ethyltin compounds).

Fig. 2. Correlation of the Coulomb integral δ(Sn) with $\Delta\tau(\tau(CH_3)-\tau(CH_2))$ of the series $(C_2H_5)_nSnCl_{4-n}$.

TABLE 1

CALCULATED PARTIAL CHARGES q(H), FOR THE METHYL PROTONS, AND CHEMICAL SHIFTS, $\tau(CH_3)$, IN SOME ORGANOTIN COMPOUNDS

Compound	$q(H)$	$\tau(CH_3)$
$(CH_3)_4Sn$	0.0300	9.90–9.96
$(CH_3)_3SnCl$	0.0330	9.34–9.39
$(CH_2)_2SnCl_2$	0.0364	8.76–8.85
CH_3SnCl_3	0.0405	8.31–8.35
$(C_2H_5)_4Sn$	0.0375	8.80–8.85
$(C_2H_5)_3SnCl$	0.0381	8.55
$(C_2H_5)_2SnCl_2$	0.0384	8.30
$C_2H_5SnCl_3$	0.0389	8.04
$(CH_3)_2Sn(CF_2CF_2H)_2$	0.0310	9.37
$[(CH_3)_3Sn]_2CH_2$	0.0298	9.94
$(CH_3)_3SnH$	0.0301	9.82
$(CH_3)_2SnH_2$	0.0301	9.80
CH_3SnH_3	0.0302	9.73
$(CH_3)_3SnCF_3$	0.0307	9.61
$(CH_3)_2SnCF_3Cl$	0.0336	9.23
$(CH_3)_3SnCCl_3$	0.0313	9.50
$(CH_3)_2SnH(CF_2CF_2H)$	0.0303	9.69
$(CH_3)_3SnCHCl_2$	0.0309	9.66
$(CH_3)_3SnCH_2Cl$	0.0305	9.78

TABLE 2

THE CALCULATED COULOMB INTEGRAL VALUES FOR THE TIN ATOM AND $\Delta\tau$ [$\tau(CH_3)$ – $\tau(CH_2)$] IN THE SERIES $(C_2H_5)_nSnCl_{4-n}$

Compound	$\delta(Sn)$	$\Delta\tau$	*Ref.*
$(C_2H_5)_4Sn$	−0.0598	−0.468	
$(C_2H_5)_3SnCl$	0.0029	0.034	
$(C_2H_5)_2SnCl_2$	0.0759	0.366	2
$C_2H_5SnCl_3$	0.1617	0.990	

lomb integral parameter δ(X) of the atom X may be considered to be a very good measure of its true electronegativity in the compound being examined, because the standard Coulomb integral parameter, δ^0 (X), is given by relation (1), in which X(X)

$$\delta^0(X) = k \cdot [X(X) - X(H)] \tag{1}$$

and X(H) are the standard electronegativities of X and hydrogen, and k is a proportionality constant. The experimental justification for this assumption is provided by the linear correlation between $\Delta\tau$ and δ(Sn) for the ethyltin compounds (Table 2 and Fig. 2). The utility of this postulate will be further demonstrated below.

(*B*). ^{13}C–*H spin–spin coupling constants in organotin compounds*

It has been shown that Fermi contact interaction is the dominant term in the spin–spin coupling interactions between two nuclei[13]. Using the Valence Bond model, the magnitude of ^{13}C–H coupling constants can be interpreted in terms of (*i*) the effective nuclear charge of the carbon atom, and (*ii*) the *s*-character in the orbitals used by the carbon atom to bond the hydrogen atom[19–21]. The dependence of $J(^{13}\text{C–H})$ on these factors is expressed quantitatively by relation (2), in which Z_{eff} is the effective

$$J(^{13}\text{C–H}) = A \cdot Z^3_{\text{eff}} \cdot \rho_s \qquad (2)$$

nuclear charge, ρ_s is the *s*-character of the carbon orbitals used to bond the hydrogen atom, and A is a constant involving gyromagnetic ratios, mean excitation energy, Planck's constant etc.

It is generally believed that the variations in $J(^{13}\text{C–H})$ are primarily due to changes in the *s*-character of the carbon orbital[11,12,19,20], although this view has been strongly criticised recently[21]. Since the Del Re calculations offer some scope for estimating contributions of the various factors influencing the magnitude of $J(^{13}\text{C–H})$, this point will be now examined in some detail.

Firstly, consider the series $\text{Me}_n\text{MCl}_{4-n}$, where M is carbon or tin, on which we have carried out Del Re type calculations. Because of the success of the Del Re calculations in correlating diverse physical properties including dipole moments and bond polarities in organotin compounds[14,15,22], the partial charges calculated by this method appear to be quite reliable. Using eqn. (7) of our previous paper[14], together with the calculated partial charges on the carbon atom, it is possible to obtain the effective nuclear charge, Z_{eff}, for the methyl carbon atom in the various compounds. The results are shown in Table 3, along with the reported values of $J(^{13}\text{C–H})$. The data given in the last column have been calculated on the basis of eqn. (2), using $(\text{CH}_3)_4\text{C}$ as reference compound to show the expected changes in the magnitude of $J(^{13}\text{C–H})$ resulting from the change in Z_{eff} alone. It is clear that variation in Z_{eff} can account for only a very small fraction of the total change, and may even be neglected in most cases. The results are consistent with the view that $J(^{13}\text{C–H})$ is primarily determined by the changes in *s*-character of the carbon orbital.

In order to examine whether the changes in the *s*-character of the carbon orbital can correlate $J(^{13}\text{C–H})$ data, isovalent hybridization arguments[23] may be applied. Isovalent hybridization arguments indicate that as X becomes more electrone-

TABLE 3

EFFECTIVE NUCLEAR CHARGE OF METHYL CARBON AND C^{13}–H COUPLING CONSTANTS IN THE SERIES $(\text{CH}_3)_n\text{MCl}_{4-n}$ (M = C or Sn)

Compound	*q(C)*	$Z_{eff.}$	$J(^{13}C\text{–}H)(Hz)$	
			Exptl.	*Calcd.*
$(\text{CH}_3)_4\text{C}$	−0.1191	3.208	124.0	124.0
$(\text{CH}_3)_3\text{CCl}$	−0.0976	3.216	127.0	124.9
$(\text{CH}_3)_2\text{CCl}_2$	−0.0726	3.225	131.8	126.0
CH_3CCl_3	−0.0433	3.235	124.2	127.2
$(\text{CH}_3)_4\text{Sn}$	−0.2500	3.162	128.0	118.8
$(\text{CH}_3)_3\text{SnCl}$	−0.2053	3.178	133.0	120.6
$(\text{CH}_3)_2\text{SnCl}_2$	−0.1537	3.196	137.8	122.7
CH_3SnCl_3	−0.0935	3.217	143.0	125.0

TABLE 4

CALCULATED COULOMB INTEGRAL VALUES δ(M) FOR THE SUBSTITUENT ATOM M (C or Sn) AND ^{13}C–H COUPLING CONSTANTS IN SOME METHYLTIN AND METHYLCARBON COMPOUNDS

Compound	$\delta(M)$	$J(^{13}C\text{–}H)(Hz)$	*Ref.*
$(CH_3)_4C$	0.1214	124	
$(CH_3)_3CCl$	0.1979	127	
$(CH_3)_2CCl_2$	0.2867	131.8	
CH_3CCl_3	0.3907	134	
$CH_3\text{–}CH_3$	0.1294	126	
CH_3CH_2Cl	0.2271	128	4, 26
CH_3CHCl_2	0.3134	131	
$(CH_3)_4Sn$	−0.0600	128	
$(CH_3)_3SnCl$	0.0032	133	
$(CH_3)_2SnCl_2$	0.0764	137.8	
CH_3SnCl_3	0.1624	143	

gative in the compound Y–A–X, more *p*-character is employed in the A–X orbital, and there is a corresponding increase in the *s*-character in the A–Y orbital. Thus, in the series $(CH_3)_nMX_{4-n}$, the *s*-character in the C–H bond of the methyl group will increase in proportion to the electronegativity of the central element M. Since the Coulomb integral parameter, δ(M), has been shown to be a good measure of the electronegativity of M, a linear correlation between $J(^{13}C\text{–}H)$ and δ(M) may be expected if the change in the *s*-character in the C–H bond is the dominating factor. The data given in Table 4, and the correlation shown in Fig. 3, confirm this view. Significantly, two separate straight lines are obtained, one for the carbon compounds and another for the tin compounds, indicating that the *s*-character in the C–M bond is determined both by the nature of the element M and by its electronegativity. Although this effect was not considered by Bent[23] in the development of isovalent hy-

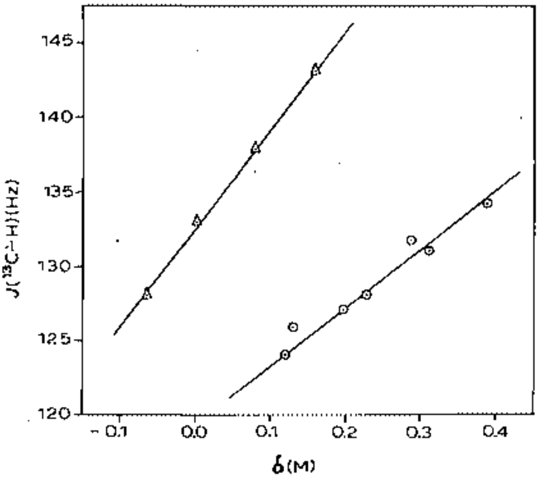


Fig. 3. Correlation of the Coulomb integral δ(M) for the substituent atom M (M = C or Sn) with $J(^{13}C\text{–}H)$ in some methyltin and methylcarbon compounds [△, methyltin compounds; ⊙, methylcarbon compounds].

bridisation schemes, it is to be expected, since the hybridisation at the carbon atom in the system $H_3C{-}M$ will depend both on the relative electronegativities of hydrogen and M and on the overlap between the carbon hybrid orbitals and those of hydrogen and M, the latter being determined by the shape and size of the valence orbital of M. A case in point is the $J(^{13}C{-}H)$ data for the compounds $(CH_3)_4C$ and $(CH_3)_4Sn$. On the basis of electronegativity alone, the s-character in the C–H bond in $(CH_3)_4C$ would be expected to be larger than that in $(CH_3)_4Sn$, and consequently $J(^{13}C{-}H)$ in $(CH_3)_4C$ should be greater than $J(^{13}C{-}H)$ in $(CH_3)_4Sn$, although the reverse order is observed. In fact, for all the compounds of the series $(CH_3)_nMCl_{4-n}$ (M = C or Sn), although $\delta(Sn)$ is always less than $\delta(C)$ in the corresponding compound, $J(^{13}C{-}H)$ is consistently higher for the tin compounds indicating that the s-character of the carbon hybrid orbital used in the C–H bond and thus the p-character in the C–Sn orbital is higher than would be expected from electronegativity alone. An important conclusion from this is that the electronegativity of a substituent atom or a group is not the only factor influencing the hybridisation, and various other factors such as interatomic overlap etc. must be taken into account.

(C). *Tin–proton spin–spin coupling constants*

The indirect tin–proton spin–spin coupling constants for the methyltin compounds have been studied by several investigators[8,10,24,25] because of their importance in the elucidation of molecular structure. As in the case of $J(^{13}C{-}H)$, the magnitude of the tin–proton coupling constants may be interpreted in terms of the effective nuclear charge on the tin atom and the s-charactor in the tin orbital used to bond to the methyl carbon atoms.

The role of the variations in the effective nuclear charge of the tin atom on tin–proton coupling constants has been investigated by using a method similar to that employed in the case of the $^{13}C{-}H$ coupling constant, and the results for the series $(CH_3)_nSnCl_{4-n}$ are shown in Table 5. They indicate that the variations in the tin–proton coupling constants expected because of changes in the effective nuclear charge of the tin atom are insignificant compared with the large observed variations, which must therefore be due to changes in the s-character in the tin–carbon bonds, as already suggested by other studies[8-10].

To examine the possibility of correlating quantitatively the tin–proton coupling constants with the s-character in the tin carbon bond, we consider the compounds

TABLE 5

EFFECTIVE NUCLEAR CHARGE ON THE TIN ATOM, AND TIN–PROTON COUPLING CONSTANTS, IN THE SERIES $(CH_3)_nSnCl_{4-n}$

Compound	*q(Sn)*	$Z_{eff.}$	$J(^{119}Sn{-}C{-}H)$ (Hz)	
			Exptl.	*Calcd.*
$(CH_3)_4Sn$	0.6400	4.374	54.0	54.0
$(CH_3)_3SnCl$	0.7066	4.397	59.7	54.9
$(CH_3)_2SnCl_2$	0.7654	4.418	71.0	55.6
CH_3SnCl_3	0.8141	4.435	100.0	56.3

$(CH_3)_nSnX_{4-n}$ (the X's are not necessarily identical). Using the isovalent hybridisation argument, the increase in the *p*-character in the Sn–X orbital will be proportional to the electronegativity of X. In the light of our discussions in the previous section, the actual change in the electronegativity of the substituent X relative to tin will be proportional to $\delta(X)-\delta(Sn)$. Therefore, the total increase in the *p*-character in the tin orbitals used in all the Sn–X bonds is proportional to $\sum[\delta(X)-\delta(Sn)]$ where the summation is over all the bonds except the tin–methyl bonds. Since the increase in the *p*-character in the Sn–X bonds will result in an equal increase in the *s*-character in the tin–methyl bonds, the net increase in the *s*-character per tin–methyl bond ($\Delta\rho_s$), relative to that in $(CH_3)_4Sn$, will be given by relation (3), in which *n* is the number of

$$\Delta\rho_s = k\cdot\sum[\delta(X)-\delta(Sn)]/n \tag{3}$$

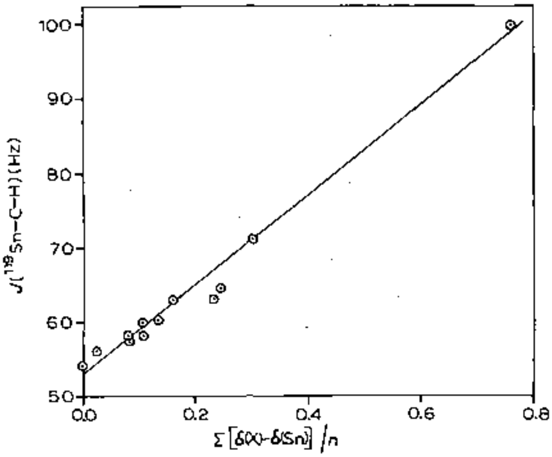
methyl groups bonded to tin and *k* is a proportionality constant. The total *s*-character in the bond will be given by eqn. (4), since the *s*-character in the tin–carbon bonds in

$$\rho_s = 0.25 + k\cdot\sum[\delta(X)-\delta(Sn)]/n \tag{4}$$

$(CH_3)_4Sn$ is 0.25 because of symmetry (sp^3 hybridisation at the tin atom). As the effective charge on the tin atom remains almost constant (Table 5), the tin–proton coupling constant, $J(Sn–C–H)$, will be given by eqn. (5), in which *B* is a constant.

$$\begin{aligned} J(Sn–C–H) &= B\cdot\rho_s \\ &= 0.25B + k\cdot B\cdot\sum[\delta(X)-\delta(Sn)]/n \end{aligned} \tag{5}$$

It is clear from eqn. (5) that a linear relation between $J(Sn–C–H)$ and $\sum[\delta(X)-\delta(Sn)]/n$ should exist if the variations in $J(Sn–C–H)$ are due to the changes in the *s*-character in the tin–methyl bonds. The calculated values of the quantity $\sum[\delta(X)-\delta(Sn)]/n$ are given in Table 6 for a number of methyltin compounds. Fig. 4 shows the correlation between $\sum[\delta(X)-\delta(Sn)]/n$ and $J(^{119}Sn–C–H)$. The linearity of the plot confirms the proposal[8-10] that the magnitude of $J(Sn–C–H)$ is a measure of the *s*-



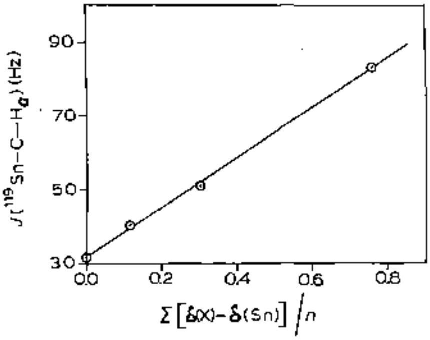


Fig. 4. Correlation between $\Sigma[\delta(X)-\delta(Sn)]/n$ and $J(^{119}Sn–C–H)$ for some methyltin compounds.

Fig. 5. Correlation between $\Sigma[\delta(X)-\delta(Sn)]/n$ and $J(^{119}Sn–C–H_\alpha)$ of some ethyltin compounds.

TABLE 6

VALUES OF $\sum[\delta(X)-\delta(Sn)]/n$ AND $J(Sn^{119}\text{–}C\text{–}H)$ IN SOME METHYLTIN COMPOUNDS

Compound	$\sum[\delta(X)-\delta Sn]/n$	$J(Sn^{119}\text{–}C\text{–}H)$ *(Hz)*	*Ref.*
$(CH_3)_4Sn$	0.0000	54.0	1, 2, 3, 27
$(CH_3)_3SnCl$	0.1160	59.7	
$(CH_3)_2SnCl_2$	0.3041	71.0	
CH_3SnCl_3	0.7578	100.0	
$(CH_3)_3SnH$	0.0272	56.5	
$(CH_3)_2SnH_2$	0.0799	58.0	
CH_3SnH_3	0.2361	63.4	
$(CH_3)_2Sn(CF_2CF_2H)_2$	0.2458	64.5	
$(CH_3)_2SnH(CF_2CF_2H)$	0.1625	62.8	
$(CH_3)_3SnCCl_3$	0.1323	60.3[a]	
$(CH_3)_3SnCHCl_2$	0.1089	58.3[a]	
$(CH_3)_3SnCH_2Cl$	0.0827	57.7[a]	

[a] These values have been calculated from the reported average values according to ref. 27.

TABLE 7

VALUES OF $\sum[\delta(X)-\delta(Sn)]/n$ AND $J(Sn^{119}\text{–}C\text{–}H_\alpha)$ IN SOME ETHYLTIN COMPOUNDS

Compound	$\sum[\delta(X)-\delta(Sn)]/n$	$J(Sn^{119}\text{–}C\text{–}H_\alpha)$ *(Hz)*
$(C_2H_5)_4Sn$	0	32.2
$(C_2H_5)_3SnCl$	0.1161	40.6
$(C_2H_5)_2SnCl_2$	0.3044	51.7
$C_2H_5SnCl_3$	0.7590	83.35

character in the tin orbital used to bond the methyl carbon atom. Although $J(^{119}Sn\text{–}C\text{–}H)$ data have been used in the correlation, a similar correlation exists with $J(^{117}Sn\text{–}C\text{–}H)$ also, because the ratio $J(^{117}Sn\text{–}C\text{–}H)/J(^{119}Sn\text{–}C\text{–}H)$ is constant.

A similar linear correlation exists between $\sum[\delta(X)-\delta(Sn)]/n$ and $J(Sn\text{–}C\text{–}H_\alpha)$ (α refers to the methylene (α) protons) in the ethyltin compounds. The relevant data are given in Table 7, and the correlation is shown in Fig. 5. Because of the considerable variation in the reported tin–proton coupling constants for the ethyltin compounds, all the data used in the present correlation have been taken from one source[2].

We conclude that, with some modifications and extensions, the Del Re method, despite the crude approximations involved in it, will prove to be a very valuable theoretical tool in the study of organotin compounds.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

V. THE CHEMICAL REACTIVITY OF ORGANOTIN COMPOUNDS

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SUMMARY

A simple reactivity index has been developed in terms of the Del Re approximations. The relative case of halodemetallation of organotin compounds in polar and non-polar solvents has been successfully explained by application of this reactivity index, it being shown that the relative rates of cleavage of the R–Sn bond in Me_3SnR, Et_3SnR and R_4Sn compounds can be correlated with the appropriate reactivity index.

INTRODUCTION

Theoretical interpretation of the reactivity of molecules is one of the principal aims of any quantum chemical model, and thus simple reactivity indices such as localization energy, frontier electron density, free valency etc. have been derived within the framework of LCAO MO theory[1–8]. However, the application of quantum mechanical reactivity theory is at present limited mainly to organic molecules, and no calculations have been carried out on organometallic compounds. Although it is possible, in principle, to extend the quantum mechanical reactivity theory of the organic compounds to organometallic compounds, such an extension is not feasible at present for several reasons, the most important being the non-availability of reliable empirical parameters needed for such calculations. However, the Del Re method, because of its extreme mathematical simplicity and its remarkable success in correlating a large number of physical properties of organotin compounds, offers an excellent means for developing simple reactivity indices for the interpretation and correlation of the chemical reactivities of organometallic compounds. In the present communication a simple reactivity index has been developed within the framework of the Del Re approximations, and has been successfully applied to the tin–carbon bond cleavage reactions in saturated organotin compounds, for which reliable Del Re parameters have been already obtained by us[9].

PROCEDURE

The quantum mechanical reactivity theory aims to predict or explain the relative ease of a given reaction, and for this purpose a simple quantum mechanical quantity, often called the "reactivity index", is employed, which is related to the activation energy of the reaction. Although the ideal reactivity index is the activation energy, the calculation of this quantity is by no means simple and drastic simplifications are usually employed. One such approach is the "isolated molecule approximation" in which the reactivity indices relate only to the property of the isolated reactant molecule. Several examples belonging to this category are total π-electron density, free valency, polarizability of the atom itself, localization energy and frontier electron density, developed for the discussion of aromatic reactions[1-7].

For a complete theoretical interpretation of reaction rates, a knowledge of the entropy term is also needed in addition to the activation energy. However, in a discussion of a group of similar reactions, the entropy term need not be considered explicitly. (The approximations involved in neglecting the entropy term have been discussed in several standard treatments on aromatic reactivity theory[10,11].) The treatment that follows is based on similar approximations, and uses the "isolated molecule approximation" in as much as only the change in the energy of the isolated reactant molecule brought about by the reagent is considered.

In the Del Re approximation, the total bond energy, E, of a saturated molecule is given[9] by eqn. (1) where all the quantities have their usual significance. Because

$$E = \sum_{\text{all bonds}} [(\delta_\mu + \delta_\nu) + \{4\varepsilon_{\mu\nu}^2 + (\delta_\mu - \delta_\nu)^2\}^{\frac{1}{2}} - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{1}$$

the bond polarity, $Q_{\mu\nu}$, is given by eqn. (2), eqn. (1) may be rewritten as in eqn. (3).

$$Q_{\mu\nu} = (\delta_\nu - \delta_\mu)/(2\varepsilon_{\mu\nu}) \tag{2}$$

$$E = \sum_{\text{all bonds}} [(\delta_\mu + \delta_\nu) + 2\varepsilon_{\mu\nu}\{1 + Q_{\mu\nu}^2\}^{\frac{1}{2}} - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{3}$$

Since $Q_{\mu\nu}$ is generally found to be small, the term, $(1+Q_{\mu\nu}^2)^{\frac{1}{2}}$, may be taken as approximately equal to $(1+\frac{1}{2}Q_{\mu\nu}^2)$, leading to the following expression:

$$E = \sum_{\text{all bonds}} [(\delta_\mu + \delta_\nu) + 2\varepsilon_{\mu\nu} + \varepsilon_{\mu\nu} \cdot Q_{\mu\nu}^2 - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{4}$$

To calculate the change in the total energy of the molecule on attack by a reagent at the μth atom, it is necessary to consider the various changes brought about in the system by this attack. Firstly, the Coulomb integral, δ_μ, of the μth atom will change from its original value because of the additional bond formed by the reagent in the transition state. This change in δ_μ will be relayed to the other atoms through the inductive parameters $\gamma_{\mu(\nu)}$. Secondly, the inductive parameters $\gamma_{\mu(\nu)}$, may themselves undergo some change from the original value. However, the changes in the inductive parameters, $\gamma_{\mu(\nu)}$, may be neglected since it is found that the same set of inductive parameters is applicable to both sp^2 and sp^3 hybridized carbon atoms[9,12], although the number of σ bonds formed by the carbon atom changes from three in the former to four in the latter. Thus the changes in energy, ΔE, may be considered in terms of a single variable δ_μ only, and may be represented approximately as in eqn. (5), where

$$\Delta E = \frac{\partial E}{\partial(\delta_\mu)} \cdot \Delta(\delta_\mu) \tag{5}$$

$\Delta(\delta_\mu)$ is the change in the Coulomb integral, δ_μ, of the μth atom. Eqn. (4), on differentiation with respect to δ_μ, gives eqn. (6). Since the Coulomb integral δ_ν is given by

$$\frac{\partial E}{\partial(\delta_\mu)} = \sum_{\text{all bonds}} \left[1 + \frac{\partial(\delta_\nu)}{\partial(\delta_\mu)} + 2\varepsilon_{\mu\nu}\cdot Q_{\mu\nu}\cdot\frac{\partial Q_{\mu\nu}}{\partial(\delta_\mu)}\right]\cdot\beta \tag{6}$$

eqn. (7)[13], any change in δ_μ will produce a first order change in δ_ν only if ν is directly attached to μ; for all other atoms the change in Coulomb integral will be insignificant

$$\delta_\nu = \delta_\nu^0 + \sum_{\text{all bonds to}\,\nu} (\gamma_{\nu(\mu)}\cdot\delta_\mu) \tag{7}$$

and may be neglected. With this approximation eqn. (6) may be rewritten as in eqn. (8),

$$\frac{\partial E}{\partial(\delta_\mu)} = \sum_\nu \left[1 + \frac{\partial(\delta_\nu)}{\partial(\delta_\mu)} + 2\varepsilon_{\mu\nu}\cdot Q_{\mu\nu}\cdot\frac{\partial Q_{\mu\nu}}{\partial(\delta_\mu)}\right]\cdot\beta \tag{8}$$

where ν signifies atoms directly bonded to the atom μ.

In the Del Re method it is always possible to express the Coulomb integral of the νth atom in terms of the Coulomb integral of the μth atom by simple algebraic manipulations, so that δ_ν may be expressed as in eqn. (9), where A_ν and $K_{\nu,\mu}$ will be

$$\delta_\nu = A_\nu + K_{\nu,\mu}\cdot\delta_\mu \tag{9}$$

independent of δ_μ, and may be found by actual Del Re calculation on the molecule. From eqn. (2) and eqn. (9) it is easy to derive eqns. (10) and (11). Combining eqns. (10),

$$\frac{\partial(\delta_\nu)}{\partial(\delta_\mu)} = K_{\nu,\mu} \tag{10}$$

$$\frac{\partial Q_{\mu\nu}}{\partial(\delta_\mu)} = (K_{\nu,\mu}-1)/(2\varepsilon_{\mu\nu}) \tag{11}$$

(11) and (8) gives eqn. (12), in which n_μ is the total number of bonds formed by the

$$\frac{\partial E}{\partial(\delta_\mu)} = \sum_\nu [1+K_{\nu,\mu}+Q_{\mu\nu}\cdot(K_{\nu,\mu}-1)]\cdot\beta = \{n_\mu - q_\mu + \sum_\nu [K_{\nu,\mu}\cdot(1+Q_{\mu\nu})]\}\cdot\beta \tag{12}$$

atom μ, and $q_\mu(=\sum_\nu Q_{\mu\nu})$ is the partial charge on the atom μ. Defining a new parameter, Z_μ, as in eqn. (13) eqns. (5), (12) and (13) taken together give the final eqn. (14).

$$Z_\mu = n_\mu - q_\mu + \sum_\nu [K_{\nu,\mu}\cdot(1+Q_{\mu\nu})] \tag{13}$$

$$\Delta E = Z_\mu\cdot\beta\cdot\Delta(\delta_\mu) \tag{14}$$

In the reactions of a group of similar compounds with a particular reagent in a given solvent, $\Delta(\delta_\mu)$ may be regarded as remaining constant throughout the series. In such cases, Z_μ will serve as a relative measure of the activation energy and hence may be regarded as a reactivity index.

RESULTS AND DISCUSSION

Although eqn. (14) is quite general, the present applications will be limited to organotin compounds only, as all the necessary Del Re parameters are available for organotin compounds[9].

The bromo- and iodo-demetallation reactions of a number of tetraalkyltins have been studied in a range of solvents[14–16]. In polar nucleophilic solvents such as methanol or acetic acid, the cleavage of the tin–carbon bond is thought to occur by an S_E2 mechanism[17]. The observed reactivity sequence for cleavage of R group in Me_3SnR is $R = Me > Et > Bu > Pr > i\text{-}Pr > t\text{-}Bu$. This steric rather than inductive sequence was unexpected, and no entirely satisfactory explanation could be offered for it. It will now be shown that this sequence can be satisfactorily explained by the newly developed reactivity index, Z_μ, both qualitatively and quantitatively.

TABLE 1

THE CALCULATED REACTIVITY INDEX $Z_{C(R)}$ AND THE EXPERIMENTAL RATE OF CLEAVAGE OF THE GROUP R IN $(CH_3)_3SnR$ TYPE COMPOUNDS BY BROMINE AND IODINE IN SOME POLAR SOLVENTS

R	$Z_{C(R)}$	k_R *I_2 in methanol*	k_R *I_2 in acetic acid*	k_R *Br_2 in acetic acid*
Methyl	5.5021	1.77	0.061	2.92
Ethyl	5.2251	0.256	0.0095	1.21
Propyl	5.2093	0.056	0.00166	0.36
Butyl	5.2092	0.132	0.00317	0.55
iso-Propyl	4.9596	0.01	0.00046	0.03
tert-Butyl	4.6880		0.00005	

TABLE 2

THE CALCULATED REACTIVITY INDEX $Z_{C(R)}$ AND THE EXPERIMENTAL RATE OF CLEAVAGE OF THE GROUP R IN $(C_2H_5)_3SnR$ TYPE COMPOUNDS BY IODINE IN METHANOL

R	$Z_{C(R)}$	k_R *I_2 in methanol*
Methyl	5.5013	3.58
Ethyl	5.2301	0.22
Propyl	5.2085	0.065
Butyl	5.2084	0.060
iso-Propyl	4.9590	0.004

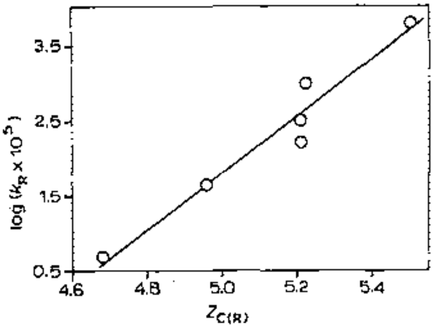
TABLE 3

THE CALCULATED REACTIVITY INDEX $Z_{C(R)}$ AND THE RELATIVE RATE OF HALODEMETALLATION OF TETRAALKYLTIN COMPOUNDS IN ACETIC ACID

Compound	$Z_{C(R)}$	k_R *(relative)* *(Br_2 in acetic acid)*	k_R *(relative)* *(I_2 in acetic acid)*
$(CH_3)_4Sn$	5.5021	100	100
$(C_2H_5)_4Sn$	5.2301	83	41
$(C_3H_7)_4Sn$	5.2087	12	4.4
$(C_4H_9)_4Sn$	5.2085	10.4	3.7
$(i\text{-}C_3H_7)_4Sn$	4.9582	2.6	0.04

If the cleavage of the group R in R'_3SnR type compounds occurs by an S_E2 process, then the appropriate reactivity index for correlating this reaction will be $Z_{C(R)}$ where C(R) signifies the carbon atom of the group R directly bonded to the tin atom. The calculated values of $Z_{C(R)}$ along with reported rate constants or relative rates $(k_R)^{14-17}$ of bromo- and iodo-demetallation in some polar solvents are given in Tables 1–3 for a number of organotin compounds. The data reveal a striking parallel between $Z_{C(R)}$ and the relative rates except for some minor perturbations with the butyl compounds.

In Figs. 1–4, the calculated values of $Z_{C(R)}$ for compounds of the type $(CH_3)_3SnR$, $(C_2H_5)_3SnR$, and R_4Sn are plotted against log k_R. As pointed out earlier, Z values can be used to correlate the reactivities of a given series of compounds towards a particular reagent under comparable conditions only. Within these restrictions which apply to all the quantum mechanical reactivity indices, Figs. 1–4 show that there is a



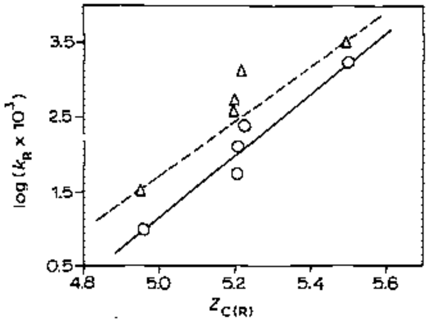
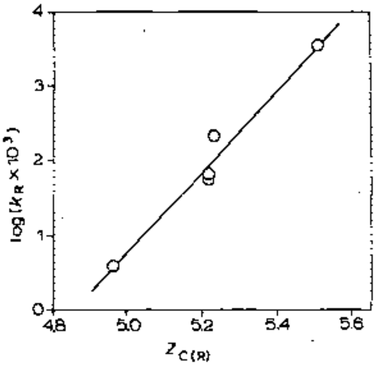


Fig. 1. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of rate of iodo-demetallation of $(CH_3)_3SnR$ compounds in acetic acid.

Fig. 2. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of the rate of halodemetallation of Me_3SnR compounds (○, iodo-demetallation in CH_3OH, △, bromo-demetallation in acetic acid.).



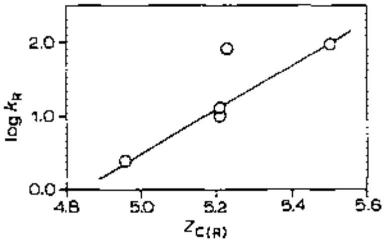


Fig. 3. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of the rate of iodo-demetallation of $(C_2H_5)_3SnR$ compounds in methanol.

Fig. 4. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of the relative rates of bromo-demetallation of R_4Sn compounds in acetic acid.

remarkably good correlation between $Z_{C(R)}$ and $\log k_R$. The existence of such linear correlation confirms the validity of the approximations involved in the derivation of the reactivity index, and also justifies the earlier suggestion that the tin–carbon bond cleavage occurs by an S_E2 process in polar solvents.

The halodemetallation reaction in less polar solvents cannot, however, be so easily correlated, since in such solvents the reagent may attack simultaneously at the carbon and tin atoms, giving rise to a cyclic S_Ei mechanism[17]. In this case the change in the energy will be given by eqn. (15). Thus no correlation is possible without the

$$\Delta E = \beta \cdot [Z_C \cdot \Delta\delta(C) + Z_{Sn} \cdot \Delta\delta(Sn)] \tag{15}$$

evaluation of actual changes in the Coulomb integrals of the carbon and the tin atoms. Further, an electrophilic attack at the carbon atom will increase $\delta(C)$ by lowering the electron density at the carbon atom, while the nucleophilic attack at the tin atom will lower $\delta(Sn)$ by increasing the electron density at the tin atom by donation. Thus $\Delta\delta(C)$ and $\Delta\delta(Sn)$ will be of opposite signs. However, some generalizations can be made by considering the extreme case in which the reaction proceeds through nucleophilic attack at the tin atom only (mechanism S_EC of ref. 17). Since the order of Z_{Sn} in R'_3SnR and R_4Sn series is R = Me > Et > Pr = Bu > i-Pr > t-Bu (Tables 4 and 5) and since $\Delta\delta(Sn)$ is negative, the expected reactivity sequence is t-Bu > i-Pr > Bu = Pr > Et > Me, in full agreement with the earlier suggestions[17].

TABLE 4

THE VALUES OF THE REACTIVITY INDEX Z_{Sn} FOR S_EC ATTACK AT THE TIN ATOM IN $(CH_3)_3SnR$ AND $(C_2H_5)_3SnR$ TYPE COMPOUNDS

$(CH_3)_3SnR$		*$(C_2H_5)_3SnR$*	
R	*Z_{Sn}*	*R*	*Z_{Sn}*
Methyl	4.0852	Methyl	4.0081
Ethyl	4.0838	Ethyl	3.9821
Propyl	4.0594	Propyl	3.9819
Butyl	4.0594	Butyl	3.9819
iso-Propyl	4.0404	iso-Propyl	3.9628
tert-Butyl	4.0253	tert-Butyl	3.9478

TABLE 5

THE CALCULATED REACTIVITY INDEX Z_{Sn} AND THE RELATIVE RATES OF BROMODEMETALLATION OF SOME TETRAALKYLTINS IN CCl_4

Compound	*Z_{Sn}*	*k_R (relative) Br_2 in CCl_4*
$(CH_3)_4Sn$	4.0852	100
$(C_2H_5)_4Sn$	3.9821	9300
$(C_3H_7)_4Sn$	3.9815	4500
$(C_4H_9)_4Sn$	3.9815	5300
$(i\text{-}C_3H_7)_4Sn$	3.9047	80000

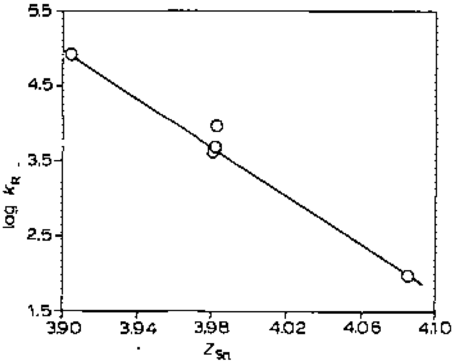


Fig. 5. Correlation between the reactivity indez Z_{Sn} and logarithm of the relative rates of bromo-demetallation in CCl_4.

Although tin–carbon bond cleavage by pure S_EC mechanism is unlikely to occur, the bromo-demetallation of R_4Sn compounds in carbon tetrachloride can be regarded as being very close to an S_EC process. This is confirmed by the linear relation between Z_{Sn} and log k_R as shown in Fig. 5. In general, however, no fixed reactivity sequence can be expected in the less polar solvents such as benzene or chlorobenzene because of the opposing effects due to the simultaneous electrophilic attack at the carbon atom and nucleophilic attack at the tin atom, and the observed sequence will be influenced by the relative magnitudes of $\Delta\delta$(C) and $\Delta\delta$(Sn) (eqn. 15), which are clearly influenced by the solvent polarity and the nature of the attacking reagent. This is again supported by experimental observations.

It is thus seen that the newly developed reactivity index provides a very satisfactory theoretical interpretation of the ease of tin–carbon bond cleavage in alkyltin compounds. In a future communication the method will be extended to unsaturated organotin compounds as well as some other organometallic molecules.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

VI. TIN–ARYL AND TIN–VINYL BOND CLEAVAGE IN TRIALKYLARYLTIN AND TRIALKYLVINYLTIN COMPOUNDS

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SUMMARY

The application of the reactivity index $Z\mu$ is extended to tin–aryl and tin–vinyl bond cleavage reactions in trialkylaryltin and trialkylvinyltin compounds. The observed reactivity sequence is interpreted, and the relative rates of tin–aryl bond cleavage in polar solvents correlated with the appropriate reactivity index.

INTRODUCTION

In a previous paper[1] a simple reactivity index was developed within the framework of the Del Re approximations, and was successfully applied to the tin–carbon bond cleavage reactions in saturated organotin compounds. In the present communication the application of this reactivity index is extended to the tin–aryl and tin–vinyl bond cleavage reactions in R_3SnAr and R_3SnVi ($R =$ alkyl group) compounds, and an explanation offered for the influence of alkyl groups on the relative rates of destannylation reactions in these compounds in both polar and non-polar solvents.

RESULTS AND DISCUSSIONS

The method of calculation of the reactivity index $Z\mu$ and the approximations involved in its formulation are given in our earlier paper[1]. The present discussion will therefore be restricted to the development of conditions under which the index $Z\mu$ may be applied to the tin–aryl or tin–vinyl bond cleavage reactions.

In aryl- and vinyltin compounds, the total energy of the molecule may be divided into two parts, *viz.*, the π-energy and the σ-energy. Hence the change in the energy of such a system due to attack by a reagent may be considered to be due to changes both in the π-energy and in the σ-energy of the molecule. The total energy change, ΔE, of the molecule may thus be written as in eqn. (1) where ΔE_π and ΔE_σ represents the changes in π- and σ-energy respectively.

$$\Delta E = \Delta E_\pi + \Delta E_\sigma \qquad (1)$$

Using eqn. (14) of our previous paper[1], eqn. (1) may be rewritten as in eqn. (2) where

Z_μ is the reactivity index and $\Delta(\delta_\mu)$ is the change in the Coulomb integral parameter of the atom, μ, being attacked by the reagent.

$$\Delta E = \Delta E_\pi + Z_\mu \cdot \beta \cdot \Delta(\delta_\mu) \tag{2}$$

If we are to use eqn. (2) directly for the study of the reactions, it is necessary to evaluate ΔE_π also. Although ΔE_π may be calculated by the Huckel LCAO MO method, it is not possible to express eqn. (2) in terms of single parameter, since the change in the Coulomb integral $\Delta(\delta_\mu)$ cannot be calculated, and is regarded as a constant for a given reaction of a group of similar compounds with a particular reagent in a given solvent[1]. However considerable simplification results if we restrict our attention to the reactions of a group of compounds containing the same aryl group, *e.g.*, trialkylphenyltin, trialkylnaphthyltin, and trialkylvinyltin compounds, under comparable conditions. In such cases the change in the π-energy ΔE_π, may be regarded as a constant throughout the series. Actual calculations using Del Re approximations for the σ-frame work and Huckel LCAO MO theory for the π-system on R_3SnAr and R_3SnVi type compounds confirm this view. It is thus expected that, in such cases, the variations in the rates of destannylation reactions will be mainly due to the variation in ΔE_σ, and the reactions may be interpreted and correlated by using the reactivity index Z_μ.

The nature of demetallation reactions in trialkylaryltin by different reagent in a number of solvents have been studied and the mechanism of the reactions has been discussed by several authors[2-9]. The reactions are found to be aromatic electrophilic substitutions, but the influence of the alkyl group upon the rate of the reactions is not very clear. The observed reactivity sequence for cleavage of the Ar–Sn bonds in R_3SnAr compounds (where Ar = phenyl, substituted phenyl, 1-naphthyl, 2-naphthyl) is R = Me > n-Bu > i-Pr when the reactions are studied in polar solvents such as methanol, isopropanol, and aqueous alcohol[2-5]. The observed decrease of the rate constants in going from Me to i-Pr has been attributed to the increase of interaction between the incoming and the leaving groups by Buchman *et al.*[2,3]. It is relevant to note that in the destannylation reactions of R_4Sn and R_3SnR' type compounds, where R and R' are alkyl groups, the observed sequence is R = Me > Et > Bu > Pr > i-Pr > t-

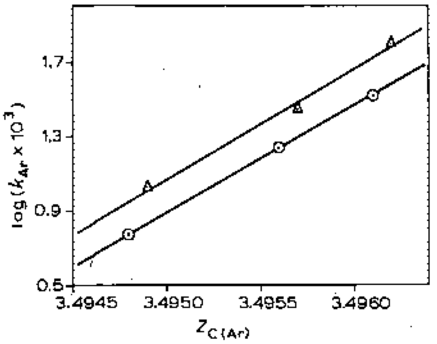
TABLE 1

REACTIVITY INDEX $Z_{C(Ar)}$ AND THE EXPERIMENTAL RATE OF CLEAVAGE OF THE GROUP Ar IN R_3SnAr TYPE COMPOUNDS BY HCl AND IODINE IN METHANOL

Compounds R_3SnAr		$Z_{C(Ar)}$	$K_2 \times 10^2$ (*HCl in methanol*)	K_2 (*I_2 in methanol*)
R	*Ar*			
Methyl	Phenyl	3.4961	3.24	437
n-Butyl	Phenyl	3.4956	1.70	107
Isopropyl	Phenyl	3.4948	0.576	15.9
Methyl	1-Naphthyl	3.4854	6.31	1100
n-Butyl	1-Naphthyl	3.4849	3.80	398
Isopropyl	1-Naphthyl	3.4841	2.24	64.6
Methyl	2-Naphthyl	3.4962	6.31	1020
n-Butyl	2-Naphthyl	3.4957	2.76	257
Isopropyl	2-Naphthyl	3.4949	1.07	28.8

Bu when the reactions are carried out in polar solvents. In our previous communication it has been shown that this sequence is mainly due to the electronic effects, the steric effects being relatively unimportant. It is therefore reasonable to expect that also in the case of R_3SnAr or R_3SnVi type compounds the steric factors will not be important in determining the sequence of the reactions.

If the mechanism of destannylation for trialkylaryltin compounds is an aromatic electrophilic substitution at the carbon atom bonded directly to the tin atom, and if we consider the reactions of the compounds having the same aryl group but different alkyl groups then the appropriate reactivity index will be $Z_{C(Ar)}$ where C(Ar) is the aryl carbon atom bonded to the tin atom. The calculated values of $Z_{C(Ar)}$ for R_3SnAr type compounds (where R = Me, n-Bu, and i-Pr and Ar = phenyl, 1-naphthyl and 2-naphthyl) are given in Table 1 along with the reported second order rate constants for iodo- and proto-destannylation reactions in methanol[2,3]. Figs. 1–4 show the



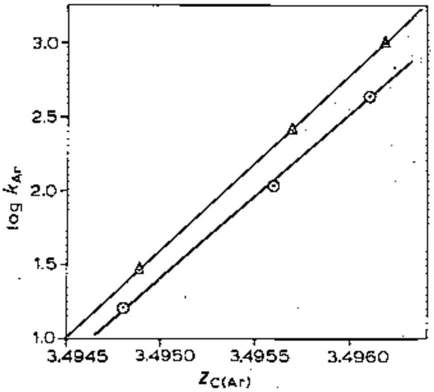
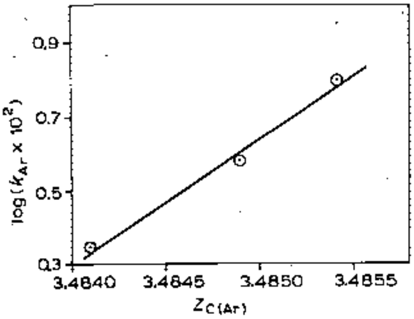


Fig. 1. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of rate of proto-demetallation of R_3SnAr type compounds in methanol; ⊙-Ar = phenyl; △-Ar = 2-naphthyl.

Fig. 2. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of rate of iodo-demetallation of R_3SnAr type compounds in methanol; ⊙-Ar = phenyl; △-Ar = 2-naphthyl.



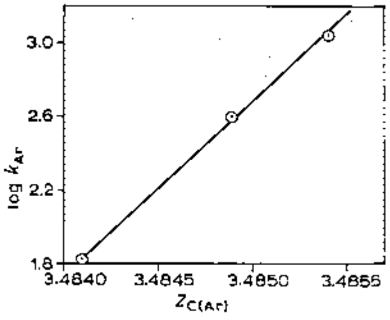


Fig. 3. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of the rate of proto-demetallation of R_3SnAr (Ar = 1-naphthyl) type compounds in methanol.

Fig. 4. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of the rate of iodo-demetallation of R_3SnAr (Ar = 1-naphthyl) type compounds in methanol.

correlation between $Z_{C(Ar)}$ and log k_{Ar}. The existence of such linear correlation between $Z_{C(Ar)}$ and log k_{Ar} strongly supports the validity of the assumptions regarding the constancy of ΔE_π in a series of R_3SnAr type compounds having the same aryl group and confirms the suggestion that the reactions are electrophilic substitutions at the carbon atom bonded to the tin atom without any appreciable nucleophilic assistance by the reagent at the tin atom. Similar arguments may be applied to the tin–vinyl bond cleavage reactions in trialkylvinyltin compounds by iodine in methanol. The calculated values of $Z_{C(Vi)}$, where C(Vi) indicates the vinyl carbon atom bonded to the tin atom, are given in Table 2. The $Z_{C(Vi)}$ values in R_3SnVi type compounds (R = Me, Et, n-Bu, i-Pr) decrease in the order Me > Et ~ n-Bu > i-Pr, which is in essential agreement with the observed reactivity sequence, *viz.*, Me ~ Et > n-Bu > i-Pr[10].

TABLE 2

VALUES OF THE REACTIVITY INDEX $Z_{C(Vi)}$ FOR SOME R_3SnVi TYPE COMPOUNDS

R in R_3SnVi	$Z_{C(Vi)}$
Methyl	3.8353
Ethyl	3.8346
Isopropyl	3.8340
n-Butyl	3.8347

In non polar solvents the demetallation reactions are difficult to interpret because of the possibility of nucleophilic assistance at the tin atom by the reagent. In such cases Z_C is no longer a valid reactivity index. As discussed in our previous paper[1], the change in the σ-energy in such cases is given by eqn. (3) and no general correlation is possible without the evaluation of actual changes in the Coulomb integrals of the carbon and the tin atoms.

$$\Delta E_\sigma = \beta \cdot [Z_c \cdot \Delta(\delta_c) + Z_{Sn} \cdot \Delta(\delta_{Sn})] \tag{3}$$

However the relative importance of the electrophilic at the carbon atom and the nucleophilic attack at the tin atom may be qualitatively evaluated in such cases by comparing the observed reactivity sequence with the two calculated extreme sequences, one for the electrophilic attack at the carbon atom, given by Z_C and the other for the nucleophilic attack at the tin atom, given by Z_{Sn}. In the iodine cleavage of $R_3SnC_6H_4X$

TABLE 3

REACTIVITY INDICES $Z_{C(Ph)}$ AND Z_{Sn} AND THE RELATIVE RATES OF IODO-DEMETALLATION OF R_3SnPh (R = Me, Et AND CYCLOHEXYL) TYPE COMPOUNDS IN CARBON TETRACHLORIDE

Compound	$Z_{C(Ph)}$	Z_{Sn}	*k(relative)* *I_2 in CCl_4*
$(CH_3)_3SnC_6H_5$	3.4961	3.9946	1
$(C_2H_5)_3SnC_6H_5$	3.4955	3.9173	5.1
$(Cyclo\text{-}C_6H_{11})_3SnC_6H_5$	3.4951	3.8581	5.4

compounds (R = cyclohexyl, Et, Me or Ph) in carbon tetrachloride, studied in detail by Bott *et al.*[7], the observed reactivity sequence is cyclohexyl > Et > Me > Ph. In Table 3 the calculated values Z_C and Z_{Sn} for some trialkylphenyltin compounds are given, along with the relative rates of tin–phenyl bond cleavage reaction. The expected sequence for purely electrophilic attack at the carbon atom in these compounds is Me > Et > cyclohexyl while that for purely nucleophilic attack at the tin is cyclohexyl > Et > Me. Since the observed reactivity sequence is the same as that expected for nucleophilic attack at the tin atom, considerable nucleophilic assistance at the tin atom by iodine is suggested in these reactions. It must however be pointed out that the observed rates do not correlate with the Z_{Sn} values, and the observed rate of cleavage of the tricyclohexyltin group is much less than what would be expected on the basis of purely nucleophilic attack (linear correlation between Z_{Sn} and log k). This suggests that the reaction is actually electrophilic in nature as suggested by Bott *et al.*, though strongly modified by the nucleophilic assistance at the tin atom by the reagent due to the non-polar nature of the solvent.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

VII. BOND POLARISABILITY INDEX AND REACTIVITY OF ORGANOTIN COMPOUNDS

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SUMMARY

Using the Del Re method a simple reactivity index, defined as the bond polarisability index, has been derived. The observed reactivity sequence for the cleavage of the alkyl groups from metalalkyls both in the polar and in the non-polar solvents have been interpreted, and the relative rates of these reactions correlated with this index. The relative rates of the exchange reactions between trialkylaluminium and trialkyltin hydrides have also been satisfactorily interpreted.

INTRODUCTION

The reactivity index Z_μ developed in our earlier papers[1,2] is a true quantum mechanical reactivity index in as much as it reflects the variation in the transition energy of the reactant molecule. However, many simple parameters, though not apparently related to the transition energy, often provide satisfactory explanations for the relative reactivity of a group of compounds under similar conditions. One such parameter is the polarisability of the metal–carbon bond in organometallic compounds, and it has been already suggested[3] that the $C \leftarrow Sn$ polarisation governs the reactivity of the alkyl groups in alkyltin compounds. This could readily be understood, since the greater the polarisability of the metal carbon bond, *i.e.*, the greater the increase in the polarity of the metal–carbon bond due to the approach of the reagent molecule, the easier will be the cleavage of the metal–carbon bond. Based on this argument, a simple reactivity index, termed the "bond polarisability index" is developed in the present communication using the Del Re approximations. Though qualitative in nature, the bond polarisability index can explain almost all the important features of tin–carbon bond cleavage reactions, and offers a simple explanation for the existence of two solvent-dependent reactivity sequences for the demetallation reactions in metal alkyls, as proposed by Abraham and Hill[4]. The relative rates of hydride exchange reaction between trialkylaluminium and trialkyltin hydrides can also be satisfactorily interpreted.

RESULTS AND DISCUSSION

In the Del Re approximation, the bond polarity, Q_{MC}, of the metal-carbon bond is given by eqn. (1) where all the quantities have their usual significance.

$$Q_{MC} = (\delta_C - \delta_M)/2\varepsilon_{MC} \tag{1}$$

As discussed in our earlier paper[1] the Coulomb integral parameters δ_C and δ_M will be changed during the course of a reaction due to the approach of the attacking reagent. This will result in a change in the metal–carbon bond polarity, the change being given by eqn. (2), where $\Delta(\delta_C)$ and $\Delta(\delta_M)$ represent the changes in δ_C

$$\Delta Q_{MC} = \frac{\partial Q_{MC}}{\partial(\delta_C)} \cdot \Delta(\delta_C) + \frac{\partial Q_{MC}}{\partial(\delta_M)} \cdot \Delta(\delta_M) \tag{2}$$

and δ_M. Expressing δ_C as a function of δ_M as in eqn. (3) where A_C and K_{CM} are independent of δ_M and using eqn. (1) it is easy to derive eqns. (4) and (5).

Combining eqns. (4), (5) and (2) gives eqn. (6)

$$\delta_C = A_C + K_{CM} \cdot \delta_M \tag{3}$$

$$\frac{\partial Q_{MC}}{\partial(\delta_C)} = (1 - 1/K_{CM})/2\varepsilon_{MC} \tag{4}$$

$$\frac{\partial Q_{MC}}{\partial(\delta_M)} = (K_{CM} - 1)/2\varepsilon_{MC} \tag{5}$$

$$\Delta Q_{MC} = [(1 - 1/K_{CM}) \cdot \Delta(\delta_C) + (K_{CM} - 1) \cdot \Delta(\delta_M)]/2\varepsilon_{MC} \tag{6}$$

In order to use eqn. (6) directly for the discussion of metal–carbon bond cleavage reactions, it is necessary to evaluate the actual changes in the Coulomb integrals of the metal atom and the carbon atom bonded to it brought about by the attacking reagent. Drastic simplification is possible, however, if we consider the electrophilic attack at the carbon atom of the alkyl group and the nucleophilic attack at the metal atom (mechanisms S_E2 and S_EC of ref. 4) separately.

In an electrophilic attack at the carbon atom by the reagent, the Coulomb integral, δ_C, of the attacked carbon atom will be primarily altered, so that ΔQ_{MC} will be given by eqn. (7). For a given metal, ε_{MC}, the metal–carbon bond resonance integral, is a constant, and $\Delta(\delta_C)$ may also be treated as constant[1] for a particular reagent in a given solvent, so that only the parameter K_{CM} governs the change in the metal–carbon bond polarity under such circumstances. Qualitatively, the increase in the metal–carbon bond polarity due to the approach of the reagent may be related to greater reactivity towards metal–carbon bond cleavage, and thus the parameter K_{CM} may be expected to correlate the reactivity of a group of similar compounds. In an electrophilic attack $\Delta(\delta_C)$ is positive due to electron withdrawal from the attacked carbon atom by the reagent[1], and an increase in K_{CM} will thus lead to greater polarisation of the bond and hence greater reactivity towards cleavage.

$$\Delta Q_{MC} = (1 - 1/K_{CM}) \cdot \Delta(\delta_C)/2\varepsilon_{MC} \tag{7}$$

For a nucleophilic attack at the metal atom similar considerations show that ΔQ_{MC} will be given by eqn. (8) and that the parameter K_{CM} determines the polarisation

$$\Delta Q_{MC} = (K_{CM} - 1) \cdot \Delta(\delta_M)/2\varepsilon_{MC} \tag{8}$$

of the metal–carbon bond in this case as well. In a nucleophilic attack, the Coulomb integral of the metal atom will be decreased because of electron donation to the metal atom through coordination by the attacking reagent so that $\Delta(\delta_{Sn})$ will be negative in sign. Therefore, an increase in K_{CM} will decrease the metal–carbon bond polarisation resulting in lower reactivity, and *vice versa*. Thus the parameter K_{CM} may be used as a reactivity index both for the nucleophilic attack and the electrophilic attack. As K_{CM} is a measure of the bond polarisation induced by the reagent, the parameter K_{CM} will be referred to hereafter as the bond polarisability index.

Demetallation reactions in metal alkyls reveal the existence of two solvent-dependent reactivity sequences[3–6]. In polar media such as methanol or acetic acid, in which the reaction is believed to proceed via electrophilic attack at the carbon atom, the relative rates of the cleavage of the group R from metal alkyls of the type RMX_n (where X may be R) follow the order Me > Et > Pr > i-Pr > t-Bu. This sequence was believed to be a steric series due to the non availability of any reactivity index for its correlation. By using the reactivity index Z_{μ}, we have already shown that, at least for the organotin compounds, the sequence is primarily determined by the variation in electronic effects, the steric factors being relatively unimportant. A comparison of the reported rate constants or relative rates $(k_R)^{3-6}$ of cleavage of the alkyl groups in a number of tetraalkyltins by different reagent in various solvents with the polarisability

TABLE 1

THE BOND POLARISABILITY INDEX K_{CSn} AND THE RELATIVE RATES OF HALODEMETALLATION OF SOME TETRALKYLTINS IN DIFFERENT SOLVENTS

Compounds	K_{CSn}	k_R *(relative)* $(Br_2$ *in AcOH*$)$	k_R *(relative)* $(I_2$ *in AcOH*$)$	k_R *(relative)* $(Br_2$ *in* $CCl_4)$
$(CH_3)_4Sn$	0.1563	100	100	100
$(C_2H_5)_4Sn$	0.1344	83	41	9300
$(C_3H_7)_4Sn$	0.1340	12	4.4	4500
$(C_4H_9)_4Sn$	0.1340	10.4	3.7	5300
$(i\text{-}C_3H_7)_4Sn$	0.1179	2.6	0.04	80000

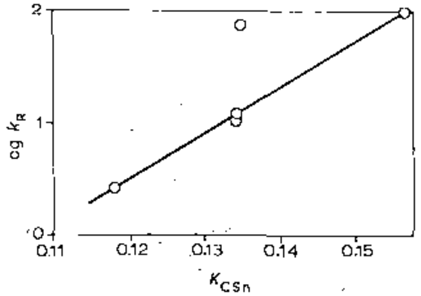
TABLE 2

THE BOND POLARISABILITY INDEX K_{CSn} AND THE EXPERIMENTAL RATES OF CLEAVAGE OF THE GROUP R IN Me_3SnR TYPE COMPOUNDS BY BROMINE AND IODINE IN SOME POLAR SOLVENTS

R	K_{CSn}	k_R $(I_2$ *in MeOH*$)$	k_R $(I_2$ *in AcOH*$)$	k_R $(Br_2$ *in AcOH*$)$
Methyl	0.1563	1.77	0.061	2.92
Ethyl	0.1344	0.256	0.0095	1.21
Propyl	0.1340	0.056	0.00166	0.36
Butyl	0.1340	0.132	0.00317	0.55
Isopropyl	0.1179	0.01	0.00046	0.03
tert-Butyl	0.1049		0.00005	

index, given in Tables 1 and 2, supports this view. Figs. 1–3 show the correlation between the polarisability index and logarithm of the rate constants, or relative rates. In agreement with the preceding discussion, the rate constant increases with the increase in the polarisability index for reactions in polar solvents, while the trend is reversed for reactions in non-polar solvents such as carbon tetrachloride. The linear correlation between the polarisability index and log k_R clearly shows that the steric factors are relatively unimportant in determining the reactivity sequence. Positive slopes of the correlation curve for reactions in polar solvents (Figs. 1 and 2) indicate electrophilic attack at the carbon atom by the reagent, while the negative slope for reactions in non-polar solvent (Fig. 3) indicates nucleophilic attack at the tin atom. The signs of the slopes are consistent with the proposed mechanisms (S_E2 and S_EC)^4.

It will now be shown that the same reactivity sequences will also be valid for the metal–alkyl bond cleavage reactions in other metal alkyls. Application of the Del Re method to a metal alkyl of the type RMX_n, shows that the bond polarisability index, K_{CM}, can be written as in eqn. (9), where the subscript ν stands for the atoms



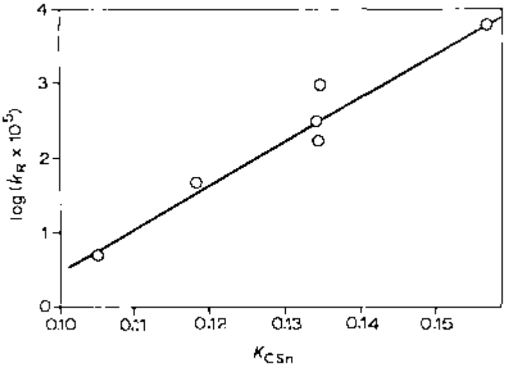


Fig. 1. Correlation between the polarisability index K_{CSn} and the logarithm of the relative rates of bromodemetallation of R_4Sn compounds in acetic acid.

Fig. 2. Correlation between the polarisability index K_{CSn} and the logarithm of the rate of iododemetallation of Me_3SnR compounds in acetic acid.

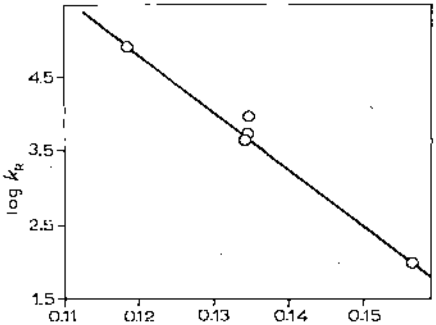


Fig. 3. Correlation between the polarisability index K_{CSn} and the logarithm of the relative rates of bromodemetallation in CCl_4.

(other than the metal atom) bound to the carbon atom of the C–M bond, the γ's are the inductive parameters, and the $K_{\nu C}$'s are given by eqn. (10). For a given metal, the inductive parameter $\gamma_{C(M)}$ is constant, so that the bond polarisability index will be pro-

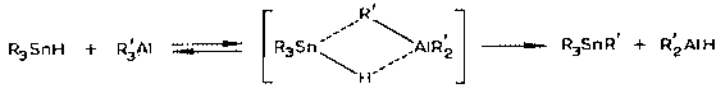
$$K_{CM} = \gamma_{CM}/[1 - \Sigma\gamma_{C(\nu)} \cdot K_{\nu C}] = f \cdot \gamma_{C(M)} \tag{9}$$

(where $f = 1/[1 - \Sigma\gamma_{C(\nu)} \cdot K_{\nu C}]$)

$$\delta_\nu = A_\nu + K_{\nu C} \cdot \delta_C \tag{10}$$

portional to the factor f which is a function of the alkyl group R only. The values of this factor for some of the alkyl groups are: Methyl, 1.563; Ethyl, 1.344; Propyl, 1.340; Butyl, 1.340; Isopropyl, 1.179; and tert-Butyl, 1.049. Provided the signs of the inductive parameter, $\gamma_{C(M)}$ for other metal–carbon bonds are the same as that for the tin–carbon bond, the reactivity sequence will be the same for all the metal alkyls. The bond polarisability index thus provides a satisfactory explanation for almost all the important features of metal–carbon bond cleavage reactions in metal alkyls.

To demonstrate the possibility of extending the bond polarisability index to the discussion of other types of reactions, we will now consider the exchange reactions between trialkyltin hydride and trialkylaluminium. These reactions are of second order and are believed to proceed through a four-centred transition state shown below[7]:



For a given trialkylaluminium, the rate of exchange can be expected to increase with increasing polarisability of the tin–hydrogen bond, because of the increase in the negativity of the hydride hydrogen. This will lead to a stronger coordination between the hydride hydrogen and the aluminium atom, which is a crucial step as shown by the fact that complexing agents, such as ethers and amines, which are capable of saturating the coordination sphere of aluminium, inhibit the exchange reaction completely[7].

Using eqns. (11) and (12), the change in the tin–hydrogen bond polarity, ΔQ_{SnH}, due to the formation of an alkyl bridge by the tin atom is given by eqn. (13). For R_3SnH type compounds K_{SnH} is given by eqn. (14). Combining eqns. (13) and (14)

$$Q_{SnH} = (\delta_H - \delta_{Sn})/2\varepsilon_{SnH} \tag{11}$$

$$\delta_{Sn} = A_{Sn} + K_{SnH} \cdot \delta_H \tag{12}$$

$$\Delta Q_{SnH} = \frac{\partial Q_{SnH}}{\partial(\delta_{Sn})} \cdot \Delta(\delta_{Sn}) = (1/K_{SnH} - 1) \cdot \Delta(\delta_{Sn})/2\varepsilon_{SnH} \tag{13}$$

and substituting the values of $\gamma_{Sn(C)}$ and $\gamma_{Sn(H)}$[8,9] gives the final eqn. (15) which shows that $Sn^{\delta+} - H^{\delta-}$ polarity will increase with increase in K_{CSn} because $\Delta(\delta_{Sn})$

$$K_{SnH} = \gamma_{Sn(H)}/[1 - 3\gamma_{Sn(C)} \cdot K_{CSn}] \tag{14}$$

$$\Delta Q_{SnH} = (1 - 0.6\,K_{CSn}) \cdot \Delta(\delta_{Sn})/2\varepsilon_{SnH} \tag{15}$$

TABLE 3

HALF-TIMES OF EXCHANGE REACTION BETWEEN TRI-n-BUTYL-ALUMINIUM AND R_3SnH TYPE COMPOUNDS AND THE POLARISABILITY INDEX K_{CSn}

R	K_{CSn}	$t_{\frac{1}{2}}$ *(min)*	*Ref.*
Ethyl	0.1344	6.2	
Propyl	0.1340	14.8	
Butyl	0.1340	14.0	7
Isobutyl	0.1337	120	
sec-Butyl	0.1175	420	
tert-Butyl	0.1049	> 10000	

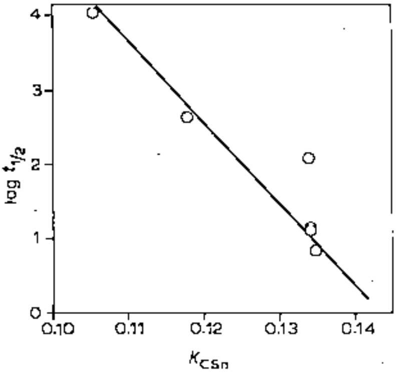


Fig. 4. Correlation between the polarisability index K_{CSn} and the logarithm of the half-times ($t_{\frac{1}{2}}$) of the exchange reaction between tri-n-butylaluminium and some trialkyltin hydrides.

is negative. For a given trialkylaluminium the rate of hydride exchange reaction will therefore be expected to increase with the increase in K_{CSn}. The data given in Table 3, and the plot in Fig. 4, in which logarithms of the half-times of the exchange reaction between tri-n-butylaluminium with some trialkyltin hydrides are used, justify this conclusion.

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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

VIII. MÖSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS

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SUMMARY

A method for calculating the electron density at the nucleus of the tin atom in a tetravalent compound has been developed using the quantities available from the Del Re calculations. The calculated electron densities show a fair correlation with the experimental Mössbauer isomer shifts, and a value of $+3.2 \times 10^{-4}$ is obtained for $(\Delta R/R)$, in excellent agreement with the value of $+3.30 \times 10^{-4}$ obtained from an independent method using internal electron conversion measurements. By defining an asymmetry parameter, A, which is a measure of the deviation of the calculated p-electron distribution from the hypothetical spherically-symmetric distribution, in which the p-electrons would be distributed equally between the three p-orbitals, the experimental quadrupole splittings have been correlated and interpreted. Factors governing the magnitude of quadrupole splitting are also discussed.

INTRODUCTION

Mössbauer spectroscopy, using the naturally occurring ^{119}Sn isotope, is being applied increasingly to the study of the nature of the bonds and the coordination number of the tin atom in organotin compounds. Much information on both isomer shifts and quadrupole splittings in organotin compounds is already available, though a satisfactory interpretation of the experimental data is not available in most cases. In some cases, a correlation between the isomer shift and the electronegativity of the substituents bound to the tin atom has been observed[1]. The relationship between the isomer shifts and tin–proton spin–spin coupling constants[2], as well as a number of theoretical approaches to the calculation of the isomer shifts in organotin compounds[3,4], have been also examined. It has been suggested that imbalance in the π-interactions determines whether or not a quadrupole splitting would be observable in an organotin compound[5,6]. This rule is, however, only qualitative, furthermore it fails in many cases[5,7–10]. 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 and the quadrupole splittings has been obtained for a number of organotin compounds[11].

However, in spite of the considerable attention given to this topic, no general approach of wide applicability has yet been developed for the interpretation and correlation of the Mössbauer parameters in organotin compounds.

Theoretically the ^{119}Sn isomer shift is linearly related to the total electron density at the tin nucleus[12], which in turn is related to the s- and p-electron populations of the valence shell[3,13]. In the present work we have therefore developed a simple method of calculating the s- and p-electron populations, and hence the electron density at the tin nucleus from the quantities available through the Del Re calculations on organotin compounds. The calculated electron densities show a fair correlation with the experimental Mössbauer isomer shifts, and the value of $(\Delta R/R)$, calculated from the correlation line, is $+3.2 \times 10^{-4}$, in excellent agreement with the value $(+3.3 \times 10^{-4})$ obtained from an independent method based on internal electron conversion measurements[14]. Moreover, a method for calculating the asymmetry in the p-electron distribution at the tin atom has been developed, and an asymmetry parameter has been defined. This parameter shows an excellent correlation with the experimental quadrupole splitting.

METHOD, RESULTS AND DISCUSSION

(*A*). *Mössbauer isomer shifts in organotin compounds*

The Mössbauer isomer shift in an organotin compound relative to a standard source is given by eqn. (1)[12,15], where $(\Delta R/R)$ is the fractional change in nuclear charge radius of the tin atom on excitation, C is a constant involving nuclear radius, charge etc., and $\Psi_a^2(o)$ and $\Psi_s^2(o)$ are the overall electron densities at the tin nucleus in the absorber and the source respectively.

$$\delta = C \cdot (\Delta R/R) \cdot [\Psi_a^2(o) - \Psi_s^2(o)] \tag{1}$$

Using relativistic wave functions for the tin atom in various oxidation states and different electronic configurations, Lees and Flinn have shown that $\Psi^2(o)$, in units of a_0^{-3}, is given by eqn. (2), where ρ_0 represents the electron density of the bare core state (Sn^{4+}), and n_s and n_p are the s- and p-electron populations of the valence shell[13].

$$\Psi^2(o) = \rho_0 + \rho \tag{2}$$

where

$$\rho = n_s(57.28 - 3.77\, n_s - 3.30\, n_p) \tag{2a}$$

Combining eqn. (1) and (2) gives eqn. (3) where C' is a constant for a given source.

$$\delta = C \cdot (\Delta R/R)\rho + C' \tag{3}$$

Eqn. (3) shows that the isomer shifts will be linearly related to ρ, which may be calculated from the s- and p-electron populations of the valence shell by eqn. (2a). In the following paragraphs we therefore develop a simple method of calculating these quantities by Del Re methods.

Consider a tetravalent tin compound. The ith hybridised valence orbital Ψ_i of the tin atom may be written as in eqn. (4), where s, p_x, p_y and p_z represent the respective atomic orbitals of the tin atom. The bonding MO, Φ_i, formed from Ψ_i and the ligand orbital Ψ_X, may be represented by eqn. (5).

$$\Psi_i = a_{is}\cdot s + a_{ix}\cdot p_x + a_{iy}\cdot p_y + a_{iz}\cdot p_z \tag{4}$$

$$\Phi_i = C_i\cdot\Psi_i + C_X\cdot\Psi_X \tag{5}$$

The electron population n_j in the jth atomic orbital ($j = s$, p_x, p_y or p_z) of the tin atom will then be given by eqn. (6)

$$n_j = \sum_i 2C_i^2\cdot a_{ij}^2 \tag{6}$$

Since the Del Re bond charge $Q_{\mathrm{Sn}i}$ for the ith tin–ligand bond is given by eqn. (7), the total electron population N, the s-electron population n_s and the total p-electron population n_p in the valence shell of the tin will be given by eqns. (8), (9) and (10) respectively.

$$Q_{\mathrm{Sn}i} = 1 - 2\,C_i^2 \tag{7}$$

$$N = \sum 2\,C_i^2 = \sum_i (1 - Q_{\mathrm{Sn}i}) = 4 - q_{\mathrm{Sn}} \tag{8}$$

$$n_s = \sum 2\,C_i^2\cdot a_{is}^2 = \sum_i (1 - Q_{\mathrm{Sn}i})\cdot\lambda_{si} \tag{9}$$

$$n_p = N - n_s = 4 - q_{\mathrm{Sn}} - \sum_i (1 - Q_{\mathrm{Sn}i})\cdot\lambda_{si} \tag{10}$$

In these eqns., $q_{\mathrm{Sn}}(=\Sigma_i Q_{\mathrm{Sn}i})$ represents the partial charge on the tin atom, and a_{is}^2 has been replaced by λ_{si}, the s-character of the ith hybridised valence orbital of the tin atom. In a previous communication[16] we have shown that for $\mathrm{Me}_n\mathrm{SnX}_{4-n}$ compounds the s-character λ_s, of the tin orbital used to bond to the methyl group is given by eqn. (11). The constant K in this eqn. can be calculated from the relation between tin–proton spin–spin coupling constants and $\Sigma(\delta_X - \delta_{\mathrm{Sn}})\,/n$.

$$\lambda_s = 0.25 + K\cdot\sum(\delta_X - \delta_{\mathrm{Sn}})\,/n \tag{11}$$

Using a value of 0.284* for K, calculated from the correlation between J(Sn–C–H) and $\Sigma(\delta_X - \delta_{\mathrm{Sn}})/n$ given in Fig. 4 of that paper[16], eqn. (11) reduces to eqn. (12) for $\mathrm{Me}_n\mathrm{SnX}_{4-n}$ (all X's identical) type compounds. For such compounds eqn. (9) also simplifies to eqn. (13), since the s-character in the Sn–X orbital will be $(1-n\cdot\lambda_s)/(4-n)$ in this case. All the parameters involved in eqn. (12) and (13) are available

$$\lambda_s = 0.25 + 0.284(4-n)(\delta_X - \delta_{\mathrm{Sn}})/n \tag{12}$$

$$n_s = n(1 - Q_{\mathrm{SnC}})\cdot\lambda_s + (1 - n\cdot\lambda_s)\cdot(1 - Q_{\mathrm{SnX}}) \tag{13}$$

from the Del Re calculations, so that n_s and hence n_p [eqn. (10)] may be easily obtained. Although the validity of eqn. (12) has been demonstrated in the case of $\mathrm{Me}_n\mathrm{SnX}_{4-n}$ type compounds only[16], we assume that the relation is true for all $\mathrm{R}_n\mathrm{SnX}_{4-n}$ type compounds as long as $\delta_X > \delta_C(\mathrm{R})$. This assumption is justified by the correlations obtained between the calculated parameters and the experimental Mössbauer isomer shifts and quadrupole splitting in a number of organotin compounds.

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* A very different value is obtained for K if one considers the correlation of the ethyl compounds given in Fig. 5 of that paper[16]. Because of considerable discrepancies in the reported values of $J(^{119}\mathrm{Sn{-}C{-}H})$ in the ethyl compounds (values as low as 32.2 Hz and as high as 69.2 Hz have been reported for $\mathrm{Et_4Sn}$) the data appear to be unreliable and are therefore not taken into account in evaluating K.

TABLE 1

CALCULATED VALUES OF THE ELECTRON POPULATION, n_s AND n_p AND THE EXPERIMENTAL MÖSSBAUER ISOMER SHIFTS

Compound	n_s	n_p	ρ in a_0^{-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	39.30	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
$PhSnCl_3$	0.849	2.314	39.43	1.27
$(Neop)_4Sn$[a]	0.840	2.519	38.48	1.34
$(Neop)_3SnCl$[a]	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

[a] Neop = $PhC(Me_2)CH_2$.

The calculated values of n_s, n_p and ρ for a number of tetravalent tin compounds for which the necessary Del Re parameters are available, are given in Table 1 along with the reported isomer shifts[15,17,18]. Fig. 1 shows the correlation between ρ and the 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. 1. In a few cases (*e.g.*, $BuSnCl_3$) the discrepancy between the values reported by different workers is so large that these points had to be omitted. It will be seen that the correlation between ρ and the isomer shift is very satisfactory, and except for only two cases out of a total of 21 compounds given in Table 1, the deviation of the experimental data from the correlation line is less than ± 0.05 mm/sec, the reported uncertainty in the isomer shift data being of the order of ± 0.1 mm/sec. This clearly demonstrates the wide applicability, as well as the reliability, of the present method.

As a further test of the reliability we have calculated the values of $(\Delta R/R)$ from the slope of the correlation line. The constant C in eqn. (1) is given by $\frac{4}{5}\pi \cdot e^2 \cdot Z \cdot R^2$, where R is the equivalent nuclear radius in the uniformly charged sphere approximation, Z is the atomic number of the Mössbauer nucleus and e, the electronic charge. Expressing the isomer shift in mm/sec, and using the value of R for tin given by Anderson *et al.*[19], this constant is calculated to be 0.85×10^{-22} for the 23.8 keV Mössbauer transition of tin. Using this value, $(\Delta R/R)$ is found to be $+3.2 \times 10^{-4}$. This value, though in excellent agreement with the value of $+3.3 \times 10^{-4}$ obtained from an independent method based on internal electron conversion[14], differs by a

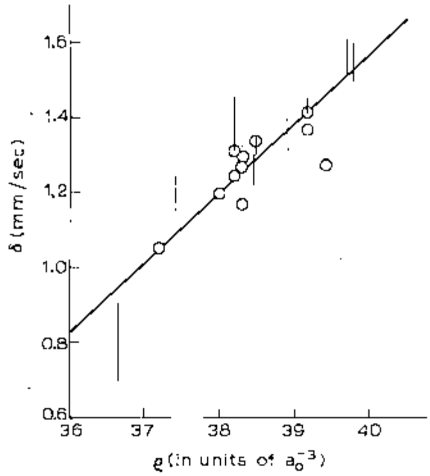

Fig. 1. Correlation between the calculated electron density ρ and the experimental isomer shift, δ.

factor of about 3 from that obtained by Lees and Flinn[13]. We 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[16,20-25], (*ii*) no assumption of doubtful validity is involved in the calculation of electron density, as is the case with most other methods*, and (*iii*) the calculated asymmetry 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 and that obtained by the direct method[14] further supports our contention.

(*B*). *Quadrupole splittings in organotin compounds*

The Mössbauer quadrupole splitting in a chemical 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 can be 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. The existence of a good linear relation between the inductive Taft constant and quadrupole splittings in a number of organotin compounds[11] indicates the asymmetry in the distribution of the *p*-electrons to be the dominating factor. In order to obtain a quantitative correlation between the asymmetry in the *p*-electron distribution and the quadrupole splittings we will first develop a method for calculating the electron population in the different *p*-orbitals of the tin atom and then define an asymmetry parameter capable of providing a quantitative measure of the deviation of the calculated electron distribution from spherical symmetry.

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* For example, Lees and Flinn considered the bonding in $[SnF_6]^{2-}$ to be purely ionic, with an ideal Sn^{4+} central ion, which is very 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. Consideration of these effects leads to an increase in the calculated values.

In a tin compound of the type Y_3SnX belonging to the point group C_{3v}, the Z-axis will be conventionally chosen along the C_3 axis (along the Sn–X bond direction). With this choice of axis, and using the normalization condition, the coefficients a_{iz}'s of the different hybrid orbitals [eqn. (4)] will be as follows:

For the hybrid orbital Ψ_1, directed along the Z axis, *i.e.*, along the Sn–X bond, $a_{1x}=a_{1y}=0$; so that a_{1z} will be given by eqn. (14). Because of the symmetry the remaining p_z-character will be equally distributed between the three remaining hybrid

$$a_{1z}=(1-a_{1s}^2)^{\frac{1}{2}} \tag{14}$$

orbitals so that:

$$a_{2z}^2=a_{3z}^2=a_{4z}^2=a_{1s}^2/3 \tag{15}$$

Using these values along with eqn. (6) and (7), it is easy to show that n_z will be given by eqn. (16), where a_{1s}^2 has been replaced by λ_{sX}, the s-character of the hybrid orbital used to bond X. Since λ_{sX} can be calculated by eqn. (12), and all other quantities

$$n_z=1+\lambda_{sX}(Q_{SnX}-Q_{SnY})-Q_{SnX} \tag{16}$$

in this eqn. are available from the Del Re calculations, n_Z can be easily obtained. Further, because of the axial symmetry in Y_3SnX molecules, the population of the p_x and p_y orbitals will be equal, and may thus be readily calculated from eqn. (17).

$$n_x=n_y=(n_p-n_z)/2 \tag{17}$$

For molecules of the type Y_2SnX_2 belonging to the point group C_{2v}, 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. 2. With this choice of axes, and using the normalization and the orthogonality conditions, the four hybridised valence orbital of the tin atom may be written as in eqns. (18a–d), where the superscripts refer to the plane in which the orbitals are located. Substituting the values of the appropriate coefficients from eqns. (18a–d) in eqn. (6) and using eqn. (7), it is easy to show that the population of the different p-orbitals will be given by eqns. (19)–(21)

$$\Psi_1^{xz}=a\cdot s+(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_x+(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot p_z \tag{18a}$$

$$\Psi_2^{xz}=a\cdot s-(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_x+(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot p_z \tag{18b}$$

$$\Psi_3^{yz}=(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot s+(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_y-a\cdot p_z \tag{18c}$$

$$\Psi_4^{yz}=(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot s-(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_y-a\cdot p_z \tag{18d}$$

where a^2 has been replaced by λ_{sX}, the s-character in the tin hybrid orbitals along the Sn-X bond. Thus, the p-electron distributions in all organotin compounds of the type

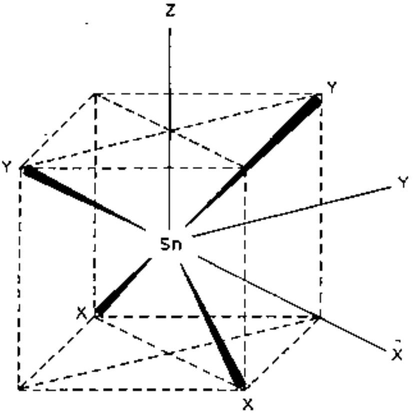
$$n_x=(1-Q_{SnX}) \tag{19}$$

$$n_y=(1-Q_{SnY}) \tag{20}$$

$$n_z=1+2\lambda_{sX}\cdot(Q_{SnX}-Q_{SnY})-Q_{SnX} \tag{21}$$

R_nSnX_{4-n} may be calculated.

Since the electrical field gradient is determined by the deviation from spherical symmetry, it is now necessary to define a parameter capable of expressing this



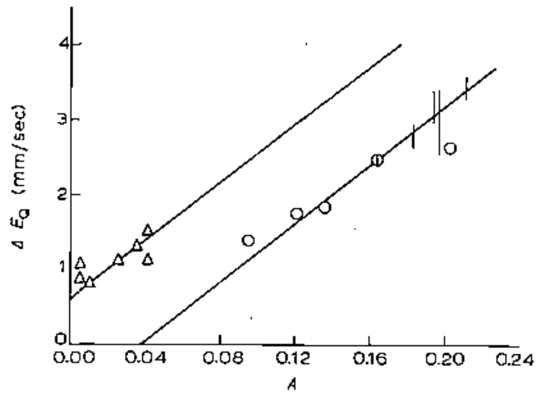


Fig. 2. Choice of coordinates in Y_2SnX_2 type compounds.

Fig. 3. Correlation between the calculated asymmetry parameter A and the experimental quadrupole splitting, ΔE_Q

deviation quantitatively. For spherical symmetry each of the three p-orbitals should have equal number of electrons, and therefore the deviation from the spherical symmetry may be quantitatively defined as the root mean square deviation of the actual electron population from the hypothetical spherically symmetric distribution, in which each of the orbitals would have $n_p/3$ electrons, as shown in eqn. (22), where n_p is the total number of electrons in the valence shell of the tin atom. We will refer to the parameter A as the asymmetric parameter, which should not be confused

$$A = [n_p/3 - n_x)^2 + (n_p/3 - n_y)^2 + (n_p/3 - n_z)^2]^{\frac{1}{2}} \tag{22}$$

with conventional asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. If the asymmetry due to the charge distributions of the ligands is very small or constant in a group of organotin compounds, then a correlation between the parameter A and the quadrupole splittings should be expected.

The calculated electron populations n_x, n_y, n_z, and the asymmetry parameters A, in a number of organotin compounds of the type R_nSnX_{4-n} are given in Table 2 along with the reported quadrupole splittings[11,17,18]. Fig. 3 shows that the compounds given in Table 2 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 another such line. The linearity of the relation between A and the quadrupole splitting, and the presence of intercepts, indicate that the asymmetry due to the ligand charge distributions around the central tin atom exert a nearly constant influence on the electrical field gradient in a given series. Both the lines shown in Fig. 3, have the same slope, suggesting that the main difference between the two groups of compounds is the magnitude of the asymmetry arising from the substituents. In the case of R_nSnX_{4-n} compounds with X = C_6F_5 or C_6Cl_5 and R = alkyl, Ph or p-tolyl, Fig. 3 shows that an appreciable contribution to the total quadrupole splitting comes from the asymmetry in the charge distributions on the substituent X, and when X is Cl or CF_3, this contribution is very small and the correlation line meets the X-axis, representing the asymmetry parameter, at about 0.04. It is noteworthy that all R_nSnX_{4-n} compounds (where R = alkyl, Ph, Vi

TABLE 2

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
$(Neop)_3SnCl$[a]	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
$Me_3Sn(C_6Cl_5)$	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

[a] Neop = $PhC(Me)_2CH_2$.

TABLE 3

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
$Me_3Sn(C_6H_4F\text{-}p)$	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

and X = Vi, Ph or *p*-substituted phenyl group) for which A is less than 0.04 do not show any quadrupole splitting (Table 3). This seems to be a general rule, the only exception being compounds having *o*-substituted phenyl groups. In this case, however, 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 the correlation we have made some preliminary calculations on $R_3SnC{\equiv}CX$ type compounds which show quadrupole splitting. However, the Del Re parameters for the *sp* carbon atom have not so far been evaluated, but since the inductive parameters do not change from sp^3 to sp^2

carbon, we have used the same inductive parameters for the *sp*-carbon atom also. On the basis of δ^0 values for sp^3 and sp^2 carbon atoms, the *sp*-carbon atom may be assigned a δ^0 value of 0.22. With these values, calculations show that for $R_3SnC{\equiv}CX$ (R = Me or Et; X = H, Me, Et, Ph and Cl) type compounds the asymmetry parameters, *A*, fall in the range 0.09–0.10 and the reported quadrupole splittings lie close to the correlation line. Although the parameters used are only approximate, and need to be refined, the asymmetry parameter *A*, will in any case be appreciably greater than 0.04, thus showing that 0.04 represents the approximate limit of the asymmetry parameter, *A*, below which quadrupole splitting will not be observed. Though no satisfactory explanation can be offered for this surprising result, it confirms and quantifies the qualitative observation of Parish and Platt[11] that a large difference in the polarities of R–Sn and Sn–X bond is necessary for quadrupole splittings, since the larger the difference in the bond polarities, the larger will be the asymmetry parameter, *A*.

Our conclusions are (*i*), that the Mössbauer isomer shifts in tetravalent organotin compounds can be interpreted in terms of 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 the charge distributions of the ligands exerts only a minor effect on the electrical field gradient.

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