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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

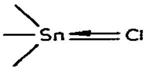
In our previous communications[1,2] we have shown that the Del Re method in conjunction with Huckel LCAO MO method can account for the heats of atomisation and dipole moments of organotin compounds with striking accuracy. In the present communication the concept of bond order has been extended to Del 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

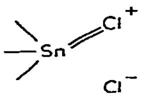
(1). *Variation in the tin–chlorine bond distance in methyltin halides*

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.

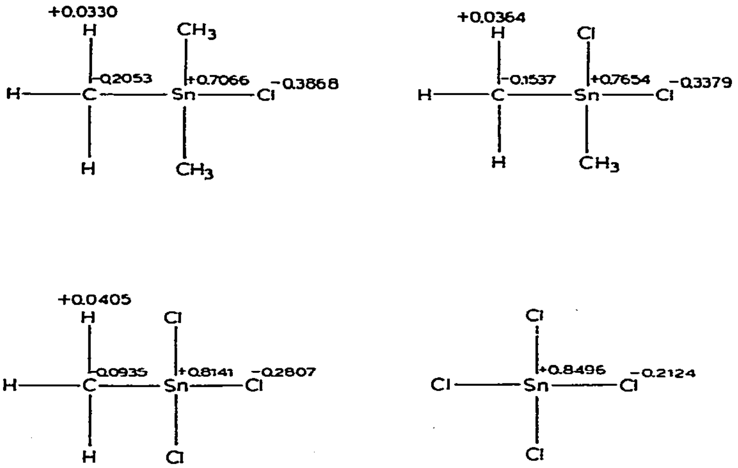


Fig. 1. Charge distributions in $Me_{4-n}Cl_n$ compounds. (a) Me_3SnCl; (b) Me_2SnCl_2; (c) $MeSnCl_3$; (d) $SnCl_4$.

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 v is written as:

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

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

$$p_{\mu v} = 2c_\mu \cdot c_v \tag{2}$$

However, it is more convenient to express the bond order in terms of bond charges $Q_{\mu v}$ 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:

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

and

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

it may be easily shown that:

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

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

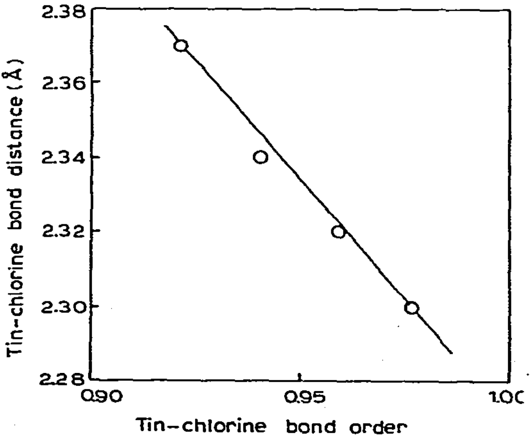


Fig. 2. Correlation between tin–chlorine bond order and tin–chlorine bond distance.

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.

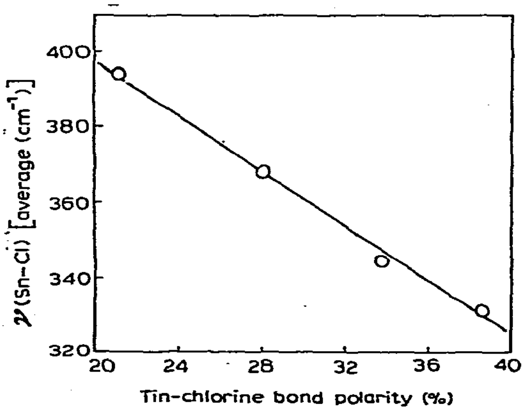


Fig. 3. Correlation between tin–chlorine bond polarity and tin–chlorine stretching frequency.

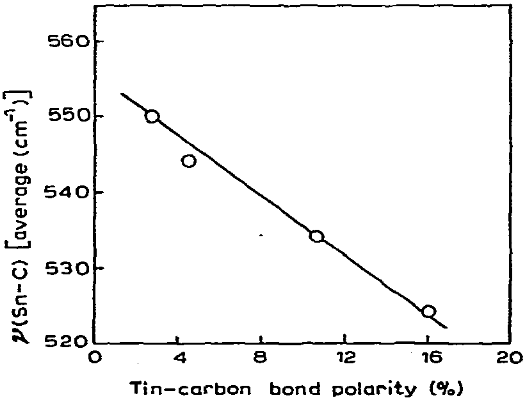


Fig. 4. Correlation between tin–carbon bond polarity and tin–carbon stretching frequency.

(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

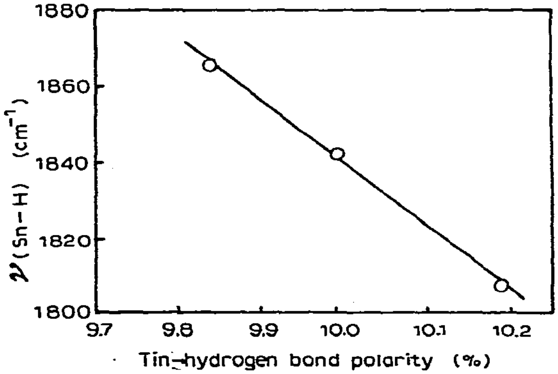


Fig. 5. Correlation between tin–hydrogen bond polarity and tin–hydrogen stretching frequencies.

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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