PREFACE

Remarkable progress has already been made by the experimental chemists in the field of organotin compounds, while new compounds are being reported, data on physical and chemical properties of these compounds are becoming increasingly available in chemical literature. However, interpretation of the experimental results are not always satisfactory and no systematic theoretical study has yet been made in this field. The present study, therefore, attempts to systematize, interprete and correlate the important physical and chemical properties of organotin compounds using simple quantum mechanical arguments and calculations based on the Del Re method. Approximations ingrained in the Del Re method are by no means satisfactory and in reality the method is a semiempirical one. Notwithstanding this, the method has been selected for the study of organotin compounds mainly because of its extreme mathematical simplicity. The Huckel LCAO MO method has also been used in conjunction with the Del Re method where a π-system is also present. The original Del Re method has been considerably extended and modified to the extent that it is now possible to interprete and correlate almost all important physical and chemical properties of organotin compounds by extremely simple "paper and pencil calculations".

In the first Chapter the Del Re method has been reviewed. Evaluation of the Del Re parameters has been discussed and the various parameters used in the present study have been tabulated.

The second Chapter deals with calculation of total bond energy of organotin compounds by the Del Re method in conjunction with the Huckel LCAO MO method where a π-system is also present. Excellent linear correlation between the calculated total bond energy and the experimental heat of atomisation is obtained. The similarity between the Del Re method for the σ-system and the Huckel LCAO MO method for the π-system has been pointed out.

The next chapter deals with the calculation of bond polarities and electric dipole moments of organotin compounds. Not only the calculated dipole moments agree with the experimental values, the calculated bond polarities are also consistent with the various experimental observations, e.g., ^{35}Cl nuclear quadrupole coupling constants, IR and bond distance data etc.

The concept of bond order has been extended to Del Re calculation in the fourth chapter. The calculated bond orders of tin-chlorine and tin-carbon bonds in $Me_{4-n}SnCl_n$ type compounds have been correlated with the experimental tin-chlorine and tin-carbon bond distances satisfactorily. Again the importance of bond polarities in determining the stretching frequencies of tin-chlorine, tin-carbon and tin-hydrogen bonds have been demonstrated by the linear correlation of the average stretching frequencies with the calculated bond polarities in a group of similar molecules.

The fifth chapter deals with the NMR spectroscopy of organotin compounds. Despite many discussions on the factors influencing, chemical shift, tin-proton and ^{13}C-H spin-spin coupling constants in organotin compounds, no general correlation of these quantities with theoretically significant parameters are yet available. An attempt has, therefore, been made to correlate the variations of chemical shifts and coupling constants with appropriate quantities obtained from Del Re calculations. It has been shown that the variation in chemical shifts of methyl protons are determined mainly by the charge on the methyl protons while the s-character, rather than the change in effective nuclear charge, determines the coupling constants in organotin compounds.

The Mossbauer spectroscopy of organotin compounds has been discussed in the next chapter. A method for calculating electron density at the tin nucleus, using the quantities available from Del Re calculations has been developed and used to correlate ^{119}Sn isomer shifts in organotin compounds. Further, a method for calculating the electron populations of the s and p orbitals of tin atom has been developed and an asymmetry parameter has been defined to correlate the quadrupole splitting data.

In the last chapter an attempt has been made to develop simple reactivity theory within the frame work of Del Re approximations. In Section A, a simple reactivity index "Z_{μ}" has been developed and applied to the interpretation of halo-demetallation reactions of saturated organotin compounds both in polar and non polar solvents. In Section B the application of this index has been extended to phenyl and vinyltin compounds. A much simpler reactivity index, the bond polarisability index, has been introduced in section C. The utility of this index in the interpretation of the reactivity of organotin compounds in particular, and organometallic compounds in general has been discussed.

The calculated charge distributions, bond polarities and other related data on some organotin compounds have also been added as an appendix.

The present study thus clearly demonstrates that the Del Re method, despite its apparent crudeness and empirical nature, will prove to be a very important and effective approach to the systemati theoretical study of organometallic compounds. Another important conclusion emerging from this investigation is that almost all the important properties of organotin compounds can be interpreted quantitatively without invoking $d_{\pi} - p_{\pi}$ bonding.