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

R. GUPTA AND B. MAJEE

Department of Chemistry, North Bengal University, District Darjeeling, West Bengal (India)

(Received January 5th, 1971)

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:

$$\begin{vmatrix} \alpha_0 + \delta_\mu \cdot \beta - E & \varepsilon_{\mu\nu} \cdot \beta \\ \varepsilon_{\mu\nu} \cdot \beta & \alpha_0 + \delta_\nu \cdot \beta - E \end{vmatrix} = 0 \quad . \tag{1}$$

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

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

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:

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

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

$$E_\sigma = \sum_{\text{all bonds}} E_{\mu\nu} \qquad (4)$$

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:

$$\alpha = \alpha_0 + h \cdot \beta_\pi \qquad \qquad (5)$$

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:

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

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:

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

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	$v_{A(B)}$	$v_{B(A)}$	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
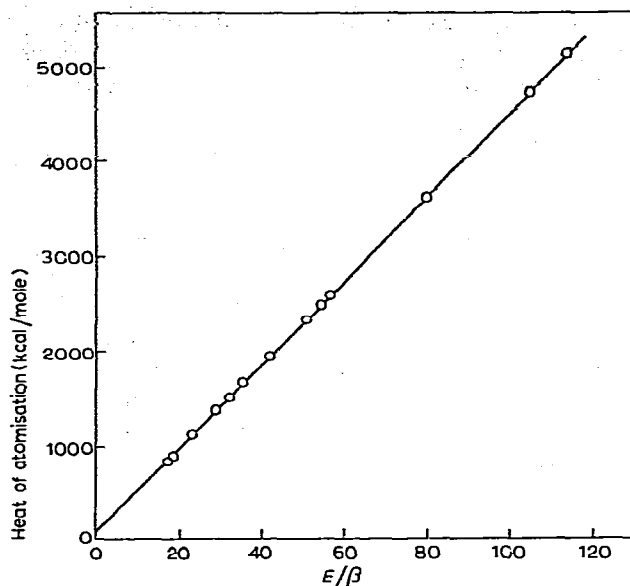
Fig. 1. Plot of the heats of atomisations of some organotin compounds *vs.* the total bond energy (calcd.) in units of β.

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.

REFERENCES

1 J. NAGY, J. REFFY, A. BORBELY–KUSZMANN AND K. B. PALOSSY, *J. Organometal. Chem.*, 17 (1969) 17.
2 J. NAGY AND P. HENCSEI, *J. Organometal. Chem.*, 20 (1969) 37.
3 J. NAGY AND J. REFFY, *J. Organometal. Chem.*, 22 (1970) 565.
4 J. NAGY AND J. REFFY, *J. Organometal. Chem.*, 20 (1970) 573.
5 J. NAGY AND J. REFFY, *J. Organometal. Chem.*, 23 (1970) 71.
6 J. NAGY AND P. HENCSEI, *J. Organometal. Chem.*, 24 (1970) 285.
7 J. NAGY AND P. HENCSEI, *J. Organometal. Chem.*, 24 (1970) 603.
8 G. DEL RE, *J. Chem. Soc.*, (1958) 4031.
9 A. ALLRED AND E. J. ROCHOW, *J. Inorg. Nucl. Chem.*, 5 (1958) 264, 269.
10 J. C. SLATER, *Phys. Rev.*, 36 (1930) 57.
11 C. A. COULSON AND A. STREITWIESER, *Dictionary of π-electron Calculation*, Pergamon, London (1965), P XII, 35.

12 J. E. LENNARD-JONES, *Proc. Roy. Soc. Ser. A*, 158 (1931) 280.
13 R. DAUDEL, R. LEFEBVRE AND C. MOSSER, *Quantum Chemistry*, Interscience, New York, 1965, p. 169.
14 R. S. MULLICEN, C. A. RIEKE, D. ORLOFF AND H. ORLOFF, *J. Chem. Phys.*, 17 (1949) 1248.
15 K. FUKUI, in O. SINNANOGLU (Ed.), *Modern Quantum Chemistry*, Part I, Academic Press, New York, 1965, p. 49.
16 H. A. SKINNER, *Advan. Organometal. Chem.*, 2 (1964) 49.
17 G. A. NASH, H. A. SKINNER AND WALLACE F. STACK, *Trans. Faraday Soc.*, 61 (1965) 508, 640–648.
18 G. W. WHELAND, *Resonance in Organic Chemistry*, Wiley, New York, 1955, p. 90.
19 A. STREITWIESER, JR., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961, Chap. 8.
20 H. EYRING, J. WALTER AND G. E. KIMBALL, *Quantum Chemistry*, Wiley, New York, 1944, p. 256.