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Electron Impact Determination of Heats of Formation and Bond Energies in Triphenyltin Compounds

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Heats of formation and bond dissociation energies for various triphenyltin compounds Ph_3Sn–R (R = Me, Et, Ph, I, SPh, Me_3Ge, Me_3Sn, Ph_3Sn) have been evaluated from appearance potential measurements

Introduction

In an earlier paper[1] relative Sn–X bond strengths in Ph_3Sn–X compounds were evaluated from appearance potential measurements, but absolute bond energies were not determined because of the lack of thermochemical data.

Results and Discussion

The appearance potentials of the Ph_3Sn^+ ion formed from a variety of triphenyltin compounds have been measured relative to that of the Et_3Sn^+ ion derived from tetraethyltin (Table I). The latter has been measured using xenon as internal standard; and hence allows absolute values for $A(Ph_3Sn^+)$ to be obtained.

$$A(Et_3Sn^+)_{Et_4Sn} = 8.70 \pm 0.09 \text{ eV}$$

Heats of formation and bond dissociation energies may be calculated if the dissociative process occurs without excess energy

$$Ph_3SnR + e \longrightarrow Ph_3Sn^+ + R^{\cdot} + 2e \qquad (1)$$

Table I. Appearance Potentials in Triphenyltin Compounds (eV)

	$A(Et_3Sn^+)_{Et_4Sn}$—$A(Ph_3Sn^+)_{Ph_3SnR}$	Absolute values ±0.2 eV *
Ph_3SnEt	0.13±0.02 (4) †	8.6
Ph_4Sn	–0.90±0.01 (4)	9.6
Ph_3SnI	0.10±0.02 (4)	8.6
Ph_3SnMe	0.04±0.01 (8)	8.7
Ph_3SnSPh	–0.31±0.03 (5)	9.0
$Ph_3SnSnPh_3$	–0.03±0.02 (8)	8.7
$Ph_3SnGeMe_3$	–0.38±0.05 (4)	9.1
$Ph_3SnSnMe_3$	–0.24±0.03 (6)	8.9

† Bracketed values-number of determinations. * Error calculated using twice the standard error of the mean for $A(Et_3Sn^+)_{Et_4Sn}$.

By Stevenson's rule[2] this assumption is probably justified if $I(Ph_3Sn^{\cdot}) < I(R^{\cdot})$. This is consistent with low abundance of R^+ relative to Ph_3Sn^+, and furthermore tailing of the ionization efficiency curves, often associated with excess energy, was only observed for Ph_3Sn^+ ions derived from metal-metal bonded compounds. Nevertheless in all cases calculated bond dissociation energies must be regarded as upper limits.

The heats of formation of triphenyltin compounds have been derived (Table II) using the relationship:

$$\Delta H_f^\circ(Ph_3SnR)_g = \Delta H_f^\circ(Ph_3Sn^+) + \Delta H_f^\circ(R) — A(Ph_3Sn^+)_{Ph_3SnR} \qquad (2)$$

Literature values of standard heats of formation used in these calculations are as follows: $CH_3 = 34 \pm 1$[3]; $C_2H_5^{\cdot} = 26 \pm 1$;[3] $PhS^{\cdot} = 50$;[3] $Me_3Sn^{\cdot} = 32 \pm 6$;[4] $I^{\cdot} = 25.54 \pm 0.05$;[5] $Ph^{\cdot} = 72 \pm 2$[3] kcal/mole^{-1}. The standard heat of formation, $\Delta H_f^\circ(Ph_3Sn^+) = 263 \pm 5$ kcal/mole^{-1} is derived from the calorimetric value of $\Delta H_f^\circ(Ph_4Sn)_g$ (114±1 kcal/mole^{-1}),[6] $A(Ph_3Sn^+)_{Ph_4Sn}$ and $\Delta H_f^\circ(Ph^{\cdot})$.

Table II. Heats of formation of triphenyltin compounds (kcal/mole^{-1})

Ph_3SnEt	91±7
Ph_3SnI	91±7
Ph_3SnMe	97±7
Ph_3SnSPh	103 *
$Ph_3SnSnMe_3$	86±9

* No error given for $\Delta H_f^\circ(PhS^{\cdot})$[3]

For the determination of Ph_3Sn–R bond energies the ionization potential of the $Ph_3Sn^{\cdot}$ radical is required, and this may be evaluated from appearance potential measurements provided $\Delta H_f^\circ(Ph_6Sn_2)_g$ is known. We have applied the Franklin group parameter method[7] to the calculation of $\Delta H_f^\circ(Ph_6Sn_2)_g$ in the following way: the ΔH_f° group value for tetravalent tin was found from the calorimetrically determined standard heats of formation for nine R_4Sn compounds[8] (38±3 kcal/mole^{-1}). Using this group

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[7] J. L. Franklin, *Ind. Eng. Chem.*, *41*, 1070 (1949).

[8] H. A. Skinner, *Adv. Organometallic Chem.*, *2*, 49 (1964).

value and those listed by Franklin the heats of formation of gaseous ethyl- and methyl-triphenyltin were estimated as 89±3 and 94±3 kcal/mole^{-1} which are in good agreement with the experimentally determined values in Table II.

Because a correction factor may apply to compounds containing a tin-tin bond, calculated heats of formation were compared with the experimentally determined values (Table III).

Table III. Calculated and measured heats of formation, $\Delta H_f°(g)$

	Calcd. kcal/mole^{-1}	Measured kcal/mole^{-1}	Difference kcal/mole^{-1}
Me_6Sn_2	15±6	−7.6±2[8]	22.6
Et_6Sn_2	−13±6	−37±3[8]	24
$Ph_3SnSnMe_3$	112±6	92±8	20

It follows that 22 kcal/mole^{-1} should be substracted from the calculated heat of formation of a ditin compound. This leads to the following values:

$$\Delta H_f°(Ph_6Sn_2)_g = 186 \pm 6 \text{ kcal/mole}^{-1}$$
$$\Delta H_f°(Ph_3Sn^\cdot) = 124 \pm 9 \text{ kcal/mole}^{-1}$$
$$I(Ph_3Sn^\cdot) = 6.0 \pm 0.4 \text{ eV}$$

and hence to the bond dissociation energies (Table IV).

Table IV. Bond dissociation energies (kcal/mole^{-1})

R	$D(Ph_3Sn—R)$	$D(Me_3Sn—R)$[4]
Me	62±10	69±6
Et	60±10	64±6
Ph	83±10	78±6
I	60±10	77±6
SPh	69±10	
$GeMe_3$	71±10	
$SnMe_3$	67±10	69±8
$SnPh_3$	62±10	

Table V. Ionization potentials

	C	Si	Ge	Sn	Pb
Me_4M	10.29[5]	9.8±0.15[10]	9.2±0.2[10]	8.25±0.15[10]	8.0±0.4[10]
$Me_3M^\cdot$	7.42[5]	7.1±0.1[9]		6.8±0.3[4]	
$Ph_3M^\cdot$	7.23[11]			6.0±0.4	

The average Sn—Ph bond strength in tetraphenyltin[6] is 61.4 kcal/mole^{-1} giving: $D(Ph_3Sn—Ph) = \bar{D}(Ph—Sn) + 22 \pm 10$ kcal/mole^{-1}. A similar relationship has been found for tetramethyltin[4]

$$D(Me_3Sn—Me) = \bar{D}(Sn—Me) + 21 \pm 4 \text{ kcal/mole}^{-1}$$

Comparison of $D(Me_3Sn—R)$[4] and $D(Ph_3Sn—R)$ shows that the strengths of tin-alkyl, tin-phenyl and tin-tin bonds are very similar for the two sets of compounds. The tin-iodine bond is significantly weaker in triphenyltin iodide; this difference may be due to steric differences in the two compounds or to a greater degree of $d\pi$—$d\pi$ interaction between Sn and I in trimethyltin iodide.

Even though $\bar{D}(M—C)$ values for group IVb organometallic compounds increase from lead to carbon,[6] the values in Table IV appear highly anomalous compared to analogous silanes.[9] Thus $D(Me_3Si—Me)$ at 76±2 kcal/mole^{-1} is only slightly greater than $D(Me_3Sn—Me)$ and $D(Ph_3Sn—Me)$. Even more surprisingly the kinetically determined Si—Si bond strength in Me_6Si_2 (67±2 kcal/mole^{-1}) is about the same as the Sn—Sn bond strength in hexamethylditin. This suggests that little quantitative significance can be attached to bond energy measurement derived from electron impact measurements unless they are supported by values determined by independent means. Ionization potentials of Me_4M, $Me_3M^\cdot$ and $Ph_3M^\cdot$ decrease in the order C>Si>Ge>Sn>Pb and, at least for C, Si and Sn in the order $Me_4M > Me_3M^\cdot > Ph_3M^\cdot$ (Table V).

Comparison with the ionization potentials of other radicals[5] [$I(CH_3^\cdot) = 9.86$; $I(Et^\cdot) = 8.80$; $I(Ph^\cdot) = 9.4$; $(I(I^\cdot) = 10.45$ eV] validates the assumption made earlier that for $Ph_3Sn—R$, $I(Ph_3Sn^\cdot) < II(R)$.

Experimental Section

Compounds were prepared as previously described.[1,12]

Appearance potentials were measured using an A.E.I. M.S.9 mass spectrometer at a source temperature of 190-210°C, trap current of 10µA and the ion repeller voltage set at a value between −1 and +5 volts during each determination. The appearance potentials of Ph_3Sn^+ ions were measured relative to $A(Et_3Sn^+)_{Et_4Sn}$ since R_3Sn^+ ions from monometallic compounds give similar ionization efficiency curves (Figure 1a) and under this condition the most accurate determinations are likely to be obtained.[13] Evaluation of a typical appearance potential by the semilogarithmic method is illustrated in Figure 1b,c.

The sensitivity of ion detection was made as great as possible by using a high source pressure ($\sim 8 \times 10^{-6}$ mm) and a resolution of only 1 part in 500. The peak heights of the two ions under investigation were equalised at an electron voltage of 50 eV by adjusting the partial pressures of the component compounds.

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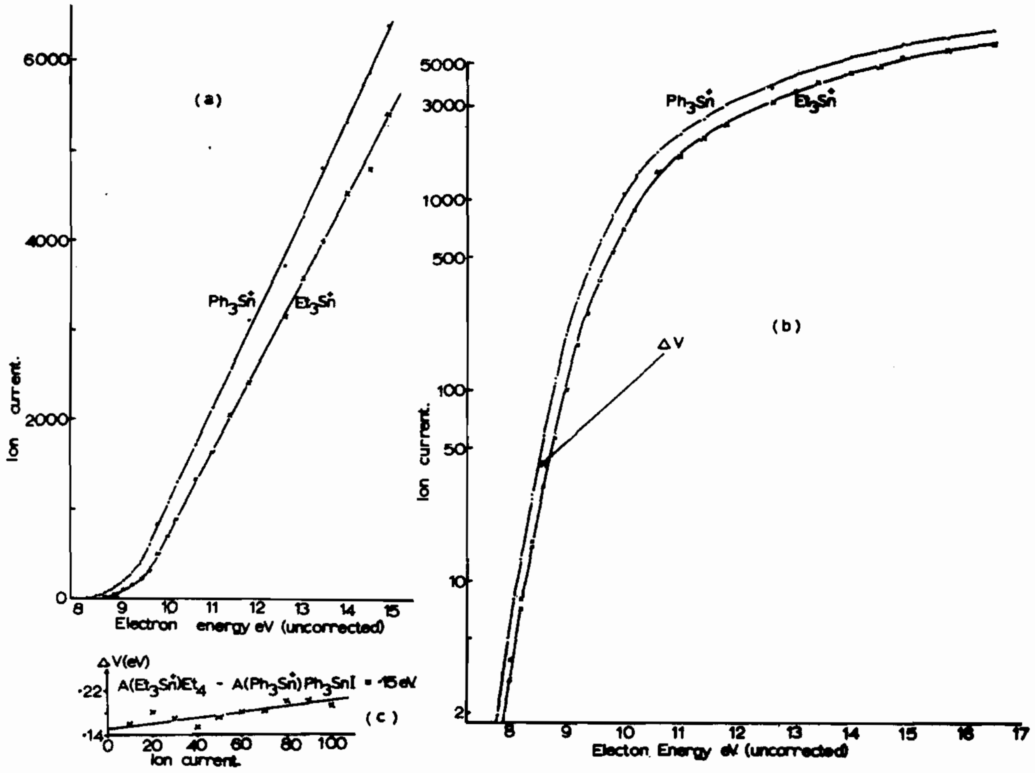

Figure 1.

At electron energies of 20 eV the ion multiplier voltage was increased to obtain maximum reading for ion collector current. The electron voltage was reduced in 0 . 2 eV steps and the currents for the two ions under investigation recorded, scanning from one peak to the other by altering the magnetic field.

Both the Warren[14] and semi-logarithmic[15] methods were used to calculate appearance potentials. Appearance potentials of Ar, N_2 and benzene measured in this way were in excellent agreement with published values.[5]

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