Thermochemistry of Metallic Alkyls

Part 13.—Heats of Redistribution Reactions of Tetra-Alkyls of Tin with Stannic Chloride

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Measurements are reported of the heats of reaction of stannic chloride with tetramethyltin, tetraethyltin, tetraethyltin and tetravinyltin in the liquid state at 25°C. The heats of these redistribution reactions are examined in terms of the bond-energy and bond-bond interaction scheme of Allen. Values are obtained for the heats of formation (as liquids) of Me₃SnCl₂, Me₂SnCl₃, Et₃SnCl and EtSnCl₃. Accepting a measured value for the first CH₃—Sn bond dissociation energy in Me₂SnCl₂ ($D_1 = 56$ kcal/mole), the thermochemistry provides the second CH₃—Sn dissociation energy ($D_2 = 32$ kcal/mole), and another example of non-equivalent stepwise dissociation energies of metal-carbon bonds.

Tetra-alkyls of tin react readily with stannic chloride on mixing the liquids together at room temperature. The reactions are exothermic, and the products are the alkyl tin chlorides, R_3SnCl , R_2SnCl_2 , and $RSnCl_3$: the amounts formed of each of these depend on the quantities of the reactants used, and the temperatures attained during reaction. The first step in reaction is the redistribution,

$$SnR_4 + SnCl_4 \rightarrow R_3SnCl + RSnCl_3,$$
(i)

which may be followed by further redistribution reactions, e.g.,

$$R_{3}SnCl + SnCl_{4} \rightarrow R_{2}SnCl_{2} + RSnCl_{3}, \qquad (ii)$$

$$RSnCl_3 + SnR_4 \rightarrow R_2SnCl_2 + R_3SnCl, \qquad (iii)$$

leading normally to a mixture of all three alkyl tin chlorides in the product. The relative amounts of the three alkyl tin chlorides in the product mixture can be determined (in favourable cases) by gas-chromatographic analysis.¹

The heats of these redistribution reactions are appreciable, and of interest theoretically in that they provide a sharp test for empirical bond-energy schemes, in particular that of Allen ² which was examined recently by Skinner and Pilcher.³

EXPERIMENTAL

COMPOUNDS.—Tetravinyl tin was a commercial sample (Fluka): samples of tetrabutyl tin, tetraethyl tin and tetramethyl tin were available from preparations made earlier ⁴ for heat of combusion studies. Stannic chloride was a commercial preparation (B.D.H. Ltd.).

CALORIMETER.—A constant temperature environment calorimeter was used. The calorimeter can A (chromium-plated copper), containing 250 ml distilled water, was supported inside a flanged brass submarine B (air-gap, 1 cm) in the thermostat bath $(25^{\circ}C)$ (fig. 1*a*). The stainless steel reaction vessel C had two compartments (one contained a weighed quantity of tetra-alkyl tin, the other a weighed amount of stannic chloride), and was sealed with an O-ring and screw top (fig. 1*b*). The reaction vessel was held upright in a cradle support inside the calorimeter, but could be turned upside down by activating the rotating mechanism. Rotation through 180° caused a glass ball to dislodge a Teflon cover slip closing the inner compartment, thus allowing the reactants to mix together.

The calorimeter contained a constant-speed stirrer, an electrical heater (for calibration of the calorimeter), and a thermistor element (Stantel F 2311/300), which served as resistance thermometer. The reaction period varied from a few minutes to upwards of half-an-hour, depending upon the reactants. When reaction had "finished" (or become very slow), the calorimeter was removed from the bath, and the products of reaction examined by gas chromatographic analysis * (Griffin katharometer detector chromatograph: silicone-oil liquid phase).

CALIBRATION.—The calorimeter was calibrated electrically by the substitution method. Heat quantities are given in thermochemical calories, $1 \text{ cal} \equiv 4.1840 \text{ abs. joule.}$





FIG. 1A.-Calorimeter with rotating reaction vessel.

FIG. 1B.-Reaction vessel.

RESULTS

TETRAVINYL TIN + STANNIC CHLORIDE

Heats of mixing of SnVn₄ with SnCl₄ in molar ratios of 1:1, 3:1 and 1:3 were measured. The products differed according to the initial molar ratio, and varied to some extent from run to run. Representing the products by the symbols $V_1(= SnVnCl_3)$, $V_2(= SnVn_2Cl_2)$ and $V_3(= SnVn_3Cl)$, the proportions normally obtained were:

1:1 mixture	80-90 % V ₂	10-5 % V ₁	10-5 % V ₃
3:1 mixture	80-70 % V ₃	$10-15 \% V_2$	10-15 % V ₁
1:3 mixture reacted	mainly as Sn	$Vn_4 + 2SnCl_4 \rightarrow V_2 + 2V_1$,	leaving $\frac{1}{3}$ of the added
SnCl ₄ unchanged.	-		

These are products of rapid mixing at 25°C. Slow mixing sometimes occurred if the cover slip disengaged badly, and led to changed relative proportions of

* The samples for analysis were separated with column temperature held at 145°C. We have assumed that further redistribution or disproportionation in the column is negligible, in view of Neumann and Burkhardt's findings with similar column conditions¹.

the products V_1 , V_2 , V_3 . The measured heats of reaction for a given mixture were generally reproducible (± 1 kcal) for rapid mixing, but slow mixing gave lower heat outputs than normal, and less complete redistribution. A typical selection from the results obtained is given in table 1.

ratio		$-\Delta H_{obs}$				
SnVn ₄ /SnCl ₄	$\overline{V_1}$	V ₂	V ₃	SnCl ₄	SnVn ₄	(kcal/mole)
1:1	5	90	5			21.0
1:1	7	85	8	<u> </u>		20.7
1:1	(33)	(33)	(33)			(16.8)
3:1		10	80		10	25.6
3:1		15	75		10	25.1
1:3	41	27		32		22.7
1:3	49	33		18	_	24.1

TABLE	1.—Heats	OF	MIXING	OF	SnVn ₄	-SnCl
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The results of table 1, together with others not listed, led to the averaged thermochemical equations below (reactants and mixture of products in the liquid state):

$$SnVn_4 + 1.01 SnCl_4 \rightarrow 0.14 V_1 + 1.75 V_2 + 0.12 V_3$$

 $\Delta H = -20.9_2 \pm 0.5 \text{ kcal/mole,} \quad (1)$

$$2.49 \text{ SnVn}_4 + \text{SnCl}_4 \rightarrow 0.51 \text{ V}_2 + 2.97 \text{ V}_3,$$

$$\Delta H = -25 \cdot 2_6 \pm 0.5 \text{ kcal/mole,} \quad (2)$$

$$SnVn_4 + 1.92 SnCl_4 \rightarrow 1.84 V_1 + 1.08 V_2$$

 $\Delta H = -23 \cdot 1_4 \pm 1.5 \text{ kcal/mole.} \quad (3)$

From these equations, the heats of the "simple" Kocheshkov redistribution reactions (iv) to (ix) were calculated :

(iv)	$SnVn_4 + SnCl_4 \rightarrow V_1 + V_3$	$\Delta H = -12.7 \text{ kcal},$
(v)	$2SnVn_4 + SnCl_4 \rightarrow V_2 + V_3$	= -24.2 kcal,
(vi)	$SnVn_4 + 2SnCl_4 \rightarrow 2V_1 + V_2$	= -23.3 kcal,
(vii)	$SnVn_4 + SnCl_4 \rightarrow 2V_2$	= -22.0 kcal,
(viii)	3 SnVn ₄ + SnCl ₄ \rightarrow 4V ₃	= -26.4 kcal,
(ix)	$SnVn_4 + 3SnCl_4 \rightarrow 4V_1$	= -24.5 kcal.

The ΔH values given for reactions (iv)-(ix) are considered uncertain within limits of $ca. \pm 3$ kcal. Part of this is due to the spread in the measured ΔH of reactions (1)-(3), and to the lack of sharpness in the analysis of the products formed: uncertainty also arises because corrections for the heats of mixing of the *products* and excess reactant in reactions (1)-(3) were not made; the latter are probably endothermic and small (~1 kcal).

Eqn. (vii), (viii) and (ix) can be used to obtain the heats of formation of the vinyl tin chlorides, in terms of the heats of formation of stannic chloride and tetravinyl tin. The recommended value for the former ⁵ is $\Delta H_f^{\circ}(\text{SnCl}_4)$, liq.) = -130.3 kcal/mole, but $\Delta H_f^{\circ}(\text{SnVn}_4, liq.)$ has not as yet been determined.* Pending measurement of the latter, we can go no further than to write:

$$\Delta H_f^{\circ}(\operatorname{Vn}_3\operatorname{SnCl}, liq) = \frac{3}{4}\Delta H_f^{\circ}(\operatorname{Vn}_4\operatorname{Sn}, liq) - 39.2 \text{ kcal/mole},$$
(4)

$$\Delta H_f^{\circ}(\operatorname{Vn}_2\operatorname{SnCl}_2, liq) = \frac{1}{2}\Delta H_f^{\circ}(\operatorname{Vn}_4\operatorname{Sn}, liq) - 76\cdot 2 \operatorname{kcal/mole},$$
(5)

$$\Delta H_{f}^{\circ}(\mathrm{VnSnCl}_{3}, liq) = \frac{1}{4} \Delta H_{f}^{\circ}(\mathrm{Vn}_{4}\mathrm{Sn}, liq) - 103.9 \text{ kcal/mole.}$$
(6)

* Measurements of the heat of combustion are now being attempted at Manchester University.

If bond energy term values were strictly constant and transferable from one molecule to another, the redistribution reactions (iv)-(ix) should all be *thermo-neutral*. On the other hand, the bond energy scheme proposed by Allen ² (in common with other schemes which relate bond energy terms to immediate molecular environment ³) permits substantial redistribution heat, because although the first-order bond energy terms involved in redistribution cancel, the second-order "bondbond" and "trio" interactions do not. Applied to the *gaseous*-phase SnR₄/SnCl₄ redistributions analogous to reactions (iv)-(ix), the Allen scheme requires that

$$\Delta H(iv) = -3x; \qquad \Delta H(v) + \Delta H(vi) = -10x; \\ \Delta H(vii) = -4x; \qquad \Delta H(viii) + \Delta H(ix) = -12x,$$

where x is a composite of bond-bond and trio interactions, viz.,

$$x = [2\alpha_{\rm RSnX} - \alpha_{\rm RSnR} - \alpha_{\rm XSnX}] + [T_{\rm R_2X} + T_{\rm RX_2} - T_{\rm R_3} - T_{\rm X_3}]$$
(7)

(The terms in α are bond-bond interactions, and terms in *T*, trio interactions: e.g., α_{RSnX} is the interaction between C—Sn and Sn—X bonds in R—Sn—X, and T_{R_2X} the interaction due to the grouping R

Using the ΔH values given above for the reactions (iv)-(ix) of SnVn₄ with SnCl₄, the derived values of x are 4.24, 4.74, 4.24 and 5.5₁ kcal, respectively (only the first and last of these are independent values). The observed ΔH refer to *liquid* reactants and products, whereas the theory requires ΔH values for the gaseous reactions. Heats of vaporization of the vinyl tin chlorides are not available, but a rough estimate of the corrections necessary to convert ΔH_{obs} to the gas phase can be made using Wheland's approximate formula,⁶ ΔH_v (25°C) = 5.4+0.036t kcal/mole, relating heat of vaporization at 25°C to normal boiling-point t°C. Applied to a redistribution reaction, e.g.,

$$\operatorname{SnR}_4(liq) + \operatorname{SnCl}_4(liq) \rightarrow \{\operatorname{R}_3\operatorname{SnCl} + \operatorname{RSnCl}_3\}(liq),$$

the gas-phase conversion is given by

$$\Delta H \text{ (gas-phase)} = \Delta H_{\text{obs.}} + 0.036 \left[\Sigma t \text{ (products)} - \Sigma t \text{ (reactants)}\right]. \tag{8}$$

The normal boiling points of the vinyl tin halides are not yet determined, but values are available for the ethyl tin halides,⁷ and we made use of the latter as the best guide to the required data: Et_4Sn , 179°C; Et_3SnCl , 210°C; Et_2SnCl_2 , 223°C; $EtSnCl_3$, 198°C; $SnCl_4$, 114°C.

Hence, for the redistribution analogous to (iv), i.e.,

$$Et_4Sn + SnCl_4 \rightarrow Et_3SnCl + EtSnCl_3$$
,

the correction amounts to 4.1 kcal, and for the redistribution analogous to (vii), i.e.,

 $Et_4Sn + SnCl_4 \rightarrow 2Et_2SnCl_2$,

is 5.5 kcal. Applying these corrections unchanged to the $SnVn_4/SnCl_4$ reactions, the gaseous-phase redistribution heats, and corresponding x values, are :

 $\Delta H(iv) = -8.6 \text{ kcal}: \qquad x = 2.9 \text{ kcal};$ $\Delta H(vii) = -16.5 \text{ kcal}: \qquad x = 4.1 \text{ kcal}.$

TETRAMETHYL TIN + STANNIC CHLORIDE

The heats of reaction of $SnMe_4$ with $SnCl_4$ in molar ratios of 1:1, 2:1, 4:1and 1:4 were measured. The 2:1 and 1:2 mixtures gave solid as well as liquid

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products, and because of this complication are not discussed further. Reactions with ratios 1:1, 4:1 and 1:4 gave liquid product only, which could be analyzed satisfactorily by gas chromatography. The observed heats of mixing of excess SnMe₄ with SnCl₄ were noticeably higher (by about 10 kcal) than in the corresponding redistribution reactions of SnVn₄. Table 2 summarizes typical results: in this table the symbol M₁ signifies MeSnCl₃, M₂ = Me₂SnCl₂ and M₃ = Me₃SnCl

SnMe ₄ /SnCl ₄		$-\Delta H_{obs}$				
ratio	M ₁	M2	M ₃	SnMe ₄	SnCl ₄	(kcal/mole)
1:1	46	17	37			23.5
1:1	42	20	38			23.1
1:1	45	17	38			22.7
4:1	3	17	42	38		35.0
4:1		15	58	27		35.3
4:1		12	57	31		37.8
1:4	34	20	9		37	28·2
1:4	31	17	8		44	27.5
1:4	41	19	6		34	29.1

These results, averaged with others not listed, led to the following representative set of thermochemical equations (reactants and mixture of products in the liquid state):

$$Me_4Sn + 1.062 SnCl_4 \rightarrow 0.907 M_1 + 0.371 M_2 + 0.784 M_3$$

 $\Delta H = -23.0 \pm 1 \text{ kcal/mole}; \quad (9)$

2.153 Me₄Sn+SnCl₄
$$\rightarrow$$
0.047 M₁+0.753 M₂+2.353 M₃,

$$\Delta H = -35.2 \pm 1.5 \text{ kcal/mole}; \quad (10)$$

 $Me_4Sn + 1.577 SnCl_4 \rightarrow 1.473 M_1 + 0.787 M_2 + 0.318 M_3,$

 $\Delta H = -29.0 \pm 1.5 \text{ kcal/mole.} \quad (11)$

These equations were used to calculate the heats of the "simple" redistribution reactions (x)-(xv), in the liquid state (no corrections for heat of mixing of products):

$SnMe_4 + SnCl_4 \rightarrow M_1 + M_3$	$\Delta H = -22.1 \text{ kcal};$	(x)
2 SnMe ₄ +SnCl ₄ \rightarrow M ₂ +2M ₃	= -33.6 kcal;	(xi)
$SnMe_4 + 2SnCl_4 \rightarrow 2M_1 + M_2$	= -33.8 kcal;	(xii)
$SnMe_4 + SnCl_4 \rightarrow 2M_2$	= -23.2 kcal;	(xiii)
$3SnMe_4 + SnCl_4 \rightarrow 4M_3$	= -43.9 kcal;	(xiv)
$SnMe_4 + 3SnCl_4 \rightarrow 4M_1$	= -44.5 kcal.	(xv)

The uncertainty in these ΔH values is estimated at from 10-15 %, for similar reasons to those already given in discussing the corresponding reactions of tetravinyltin. On combining equations (xiii), (xiv) and (xv) with available heats of formation for liquid stannic chloride ⁵ and tetramethyltin ⁴ (ΔH_f° (Me₄Sn, liq) = -12.53 ± 0.5 kcal/mole), the heats of formation of M₁, M₂ and M₃ may be calculated : *

$$\Delta H_{f}^{\circ}(\text{Me}_{3}\text{SnCl}, liq) = -53.0 \pm 3 \text{ kcal/mole};$$
(12)

$$\Delta H_f^{\circ}(\text{Me}_2\text{SnCl}_2, liq) = -83.1 \pm 5 \text{ kcal/mole};$$
(13)

$$\Delta H_f^{\circ}(\text{MeSnCl}_3, liq) = -112.0 \pm 3 \text{ kcal/mole.}$$
(14)

* The liquids would in some cases be "supercooled" at 25°C, e.g., Me₂SnCl₂ has m.p. = 108°C.

To convert the redistribution heats from the liquid to the gas phase, we have used the following b.p.: Me₄Sn, 78°C; Me₃SnCl, 153°C; Me₂SnCl₂, 188°C; and MeSnCl₃, 180°C. Hence, for the gas-phase redistribution,

$Me_4Sn + SnCl_4 \rightarrow M_3 + M_1$,	$\Delta H = -17.0 \text{ kcal/mole},$ x = 5.7 kcal;	(\mathbf{x}, g)	
$Me_4Sn + SnCl_4 \rightarrow 2M_2$,	$\Delta H = -16.6$ kcal/mole,	(xiii, <i>q</i>)	

x = 4.2 kcal.

and

Measurements were made of the heats of mixing of SnEt₄ with SnCl₄ in molar ratios 1:1, 3:1 and 1:3. Averaged results are summarized in table 3, where $E_1 = \text{EtSnCl}_3$, $E_2 = \text{Et}_2\text{SnCl}_2$ and $E_3 = \text{Et}_3\text{SnCl}$.

	TABLE 3	-HEATS OF	MIXING OF S	SnEt ₄ with	SnCl ₄	
S-TH /S-CI	products (% of total)					
SnEt ₄ /SnCl ₄	E ₁	E ₂	E ₃	SnEt ₄	SnCl ₄	(kcal/mole)
1:1	46	3	51			$23 \cdot 0 \pm 1$
3:1	23	2	27	48		$22 \cdot 3 \pm 1$
1:3	33	8	17	_	42	25·4±2

These results correspond to the following set of thermochemical equations (reactants and products in the liquid state, products mixed together):

SnEt₄+0.95 SnCl₄
$$\rightarrow$$
0.90E₁+0.05E₂+1.00E₃
1.09 SnEt₄+SnCl₄ \rightarrow 0.91E₁+0.09E₂+1.09E₃
SnEt₄+1.33 SnCl₄ \rightarrow 1.33E₁+0.33E₂+0.67E₃
 $\Delta H = -23.0 \pm 1$ kcal; (15)
 $\Delta H = -22.3 \pm 1$ kcal; (16)

In contrast to the redistribution reactions of tetravinyltin and tetramethyltin, the tetraethyltin reactions do not readily proceed beyond the first stage at room temperature. Thus, addition of $SnEt_4$ in excess of 1:1 produced a result only slightly different from the 1:1 mixture, but addition of excess SnCl₄ led to some further reaction $(E_3 + \text{SnCl}_4 \rightarrow E_2 + E_1)$. The similarity of eqn. (15) and (16) makes it impracticable to solve the set fully, as was done for SnVn₄ and SnMe₄ redistributions. However, by adding (15) to (16), and combining with (17) to eliminate E_2 , we obtain :

 $1.2 \text{ SnEt}_4 + \text{SnCl}_4 \rightarrow 0.9\text{E}_1 + 1.3\text{E}_3$

 $\Delta H = -24.9 \pm 1.2 \text{ kcal/mole}, \quad (18)$

which may be written as the sum of $0.9 \operatorname{SnEt}_4 + 0.9 \operatorname{SnCl}_4 \rightarrow 0.9 \operatorname{E}_1 + 0.9 \operatorname{E}_3$

and

 $0.3 \text{ SnEt}_4 + 0.1 \text{ SnCl}_4 \rightarrow 0.4\text{E}_3$

 $\Delta H = 0.1 \Delta H(xvii)$ (20)

where $\Delta H(xvi)$ and $\Delta H(xvii)$ refer to the simple redistribution reactions

(xvi) $SnEt_4 + SnCl_4 \rightarrow E_1 + E_3$ (xvii) $3SnEt_4 + SnCl_4 \rightarrow 4E_3$.

$$\Delta H = -23.0 \pm 1 \text{ kcal};$$
 (15)

$$\Delta H = -25.4 \pm 2 \text{ kcal.} \quad (17)$$

$$\Delta H = 0.9 \ \Delta H(\text{xvi}), \quad (19)$$

(19)

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The Allen scheme leads us to expect that $\Delta H(xvii)$ should be of the order *twice* $\Delta H(xvi)$: accepting this, it follows from (18), (19) and (20) that

$$\cdot 9 \Delta H(xvi) + 0.1 \Delta H(xvii) = 1.1 \Delta H(xvi) = -24.9 \pm 1.2 \text{ kcal/mole}$$

whence $\Delta H(xvi) = -22.6 \pm 1.1$ kcal/mole, and $\Delta H(xvii) = -45.3 \pm 2.2$ kcal/mole. The latter, combined with the available heat of formation of tetraethyltin (ΔH_f° (SnEt₄, *liq*) = -22.9 ± 0.6 kcal/mole) gives ΔH_f° (Et₃SnCl, *liq*) = -61.1 kcal/mole. In conjunction with $\Delta H(xvi)$, this in turn provides ΔH_f° (EtSnCl₃, *liq*) = 114.7 kcal/mole. Both these derived heats of formation depend on the validity of the assumption made on the basis of the Allen scheme, and the ΔH_f° values should be regarded as "provisional" only.

On correction of $\Delta H(xvi)$ to the gas phase reaction, we obtain $\Delta H = -18.5$ kcal/mole, so that x = 6.2 kcal.

TETRABUTYLTIN AND STANNIC CHLORIDE

Heats of mixing of $\text{SnBu}_4/\text{SnCl}_4$ were measured with molar ratios of 1:1, 3:1 and 1:3. However, addition of excess SnBu_4 or SnCl_4 relative to the 1:1 mixture made little change, and at calorimeter temperature (25°C) it seems that reaction does not proceed, other than very slowly, beyond the first stage. The V.P.C. analyses confirmed this, little trace of Bu_2SnCl_2 being detected in the products. Moreover, on mixing Bu_3SnCl with SnCl_4 in the calorimeter there was no significant evolution of heat: similarly on mixing BuSnCl_3 with SnBu_4 . The results obtained are summarized in table 4.

TABLE 4.—HEATS OF MIXING OF SnBu4 WITH SnCl4

molar ratio, SnBu ₄ /SnCl ₄	$-\Delta H_{obs.}$ (kcal/mole)
1:1	$22 \cdot 1 \pm 0 \cdot 3$
3:1	20.7 ± 0.5
1:3	20.3 ± 0.3

The differences in $\Delta H_{obs.}$ for the 1:1, 3:1 and 1:3 mixtures are considered mainly due to the solution heats of products in excess reactants. The $\Delta H_{obs.}$ for the 1:1 mixture is attributed to the simple liquid redistribution reaction:

$$SnBu_4 + SnCl_4 \rightarrow Bu_3SnCl + BuSnCl_3$$
, (xviii)

and compares closely with the heats derived for the similar reaction of $SnMe_4$ (eqn. (x)) and of $SnEt_4$ (eqn. (xvi)).

DISCUSSION

Previous direct measurements of the redistribution heats of metal alkyl/metal halide reactions are restricted to those of mercury alkyls with mercuric halides, discussed by Pritchard and Skinner.⁸ These redistributions, as in the present case, are also markedly exothermic, e.g., the gaseous phase redistribution HgMe₂+HgCl₂ \rightarrow 2MeHgCl has $\Delta H = -13.6$ kcal/mole. Moreover, the heats of redistribution vary according to the nature of the alkyl radical, and seem to correlate with the "electronegativity" of the radical transferred. Skinner and Pritchard noted that the redistributions HgR₂+HgX₂ \rightarrow 2RHgX tend to be more exothermic the larger the difference between the electronegativities of R and X. The present studies have shown that the x values for R = Me, Et and Bu are significantly larger than that for R = vinyl, which fits in with the placing of the vinyl group as electronegative ⁹ relative to n-alkyl groups. On the other hand, the interpretation of x

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in terms of the Allen scheme shows it to be a complex of bond-bond and "trio" interactions (eqn. (7)), and its connection with electronegativity is somewhat obscure. If the trio interactions in eqn. (7) are ignored, so that $x = 2\alpha_{RSnX} - (\alpha_{XSnX} + \alpha_{RSnR})$, then for $x(R = R_1)$ to be larger than $x(R = R_2)$, it is necessary *either* that $\alpha_{R_1SnX} > \alpha_{R_2SnX}$ or that $\alpha_{R_2SnR_2} > \alpha_{R_1SnR_1}$. Since x (R = Me, Et) is significantly larger than x (R = vinyl), this implies either that there is more stabilization arising from C—Sn—X interactions when C belongs to CH₃ than to —CH = CH₂, or (conversely), that more stabilization arises from C—Sn—C interactions when C belongs to $-CH = CH_2$ than when it belongs to CH₃. The latter possibility would be consistent with some degree of π -conjugation between vinyl groups, via the Sn atom, in tetravinyltin, and in tri- and divinyltin compounds. If the former is the important factor, the stabilization is presumably "ionic-covalent" in origin, increasing the more readily the radical R in R—Sn—X releases electrons in response to demand from the polar Sn—X bond. The inference is that α_{RSnX} increases the more electropositive the radical R.

The values now reported for the heats of formation of alkyltin chlorides add substantially to the otherwise meagre data currently available on organotin halides. For convenient inspection, these are collected together in table 5.

TABLE 5.—AVAILABLE	ΔH_f°	VALUES	FOR	ORGANOTIN	HALIDES
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compound	ΔH_f° (kcal/mole)	method	ref.
Me ₃ SnCl (<i>liq</i>)	-53.0 ± 3	SnMe ₄ /SnCl ₄	this paper
Me ₃ SnBr (<i>liq</i>)	-44.9 ± 1	$SnMe_4/Br_2$	(10)
Me ₃ SnI (<i>liq</i>)	-31.8 ± 1	Sn_2Me_6/I_2	(10)
Et ₃ SnCl (liq)	(-61.1)	SnEt ₄ /SnCl ₄	this paper
Bu ₃ SnBr (<i>liq</i>)	-85.5 ± 2	$SnBu_4/Br_2$	(11)
$Ph_3SnBr(c)$	$+47.7\pm4$	Ph_3SnBr/Br_2	(11)
Me_2SnCl_2 (<i>liq</i>)	-83.1 ± 5	SnMe ₄ /SnCl ₄	this paper
$Ph_2SnBr_2(c)$	-0.4 ± 3	Ph ₄ Sn/Br ₂	(11)
MeSnCl ₃ (liq)	-112.0 ± 3	SnMe ₄ /SnCl ₄	this paper
EtSnCl ₃ (liq)	(-114.7)	SnEt ₄ /SnCl ₄	this paper

The determination of $\Delta H_{f}^{\circ}(\text{Me}_{2}\text{SnCl}_{2})$ is of interest in relation to the studies by Price and Trotman-Dickenson ¹² on the kinetics of pyrolysis of dimethyltin dichloride, using the toluene carrier-gas technique, from which they obtained the dissociation energy of the first CH₃—Sn bond, $D_{1} = D(\text{Me}-\text{SnMeCl}_{2}) = 56\cdot1$ kcal/mole. Combining the measured $\Delta H_{f}^{\circ}(\text{Me}_{2}\text{SnCl}_{2}, lig) = -83\cdot1\pm5$ kcal/mole with an estimated ${}^{6} \Delta H_{\text{vap}} = 12\cdot1$ kcal/mole to give $\Delta H_{f}^{\circ}(\text{Me}_{2}\text{SnCl}_{2}, g) = -71\cdot0\pm5$ kcal/mole, and accepting the recommended values $\Delta H_{f}^{\circ}(\text{CH}_{3}, g) = 33\pm1$ kcal/ mole ¹³ and $\Delta H_{f}^{\circ}(\text{SnCl}_{2}, g) = -49\pm2$ kcal/mole,¹⁴ the sum of both CH₃—Sn bond dissociation energies in Me₂SnCl₂ is readily calculated :

$$Me_2SnCl_2(g) \rightarrow 2CH_3(g) + SnCl_2(g),$$

$$\Delta H = 88(\pm 6) \text{ kcal/mole} = (D_1 + D_2).$$

Hence the first dissociation energy D_1 is decidedly larger than the second ($D_1 = 56$, $D_2 = 32$). A similar situation applies in the dialkyls of mercury, cadmium and zinc,¹⁵ where in each case $D_1 > D_2$.

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