AD 295 156

The Victoria University of Manchester

Manchester 13, England.

FTR No.1, 30-9-62.

The Thermochemistry of Tin Alkyls : The Heats of Combustion of Tin tetramethyl, Tin tetraethyl and Trimethylethyl tin.

Contract No. DA-91-591-EUC-1748 01-7569-61

Period : Oct. 1, 1961 - Sept. 30, 1962.

Investigators: J.V. Davies and H.A. Skinner.

The research reported in this document has been made possible through the support and sponsorship of the U.S. Department of Army, through its European Research Office.

1. Introduction

The thermochemistry of the tin alkyls has not commanded a lot of attention to-date, and the few heat of formation data on tin alkyls so far reported are not in good agreement with one another. Heat of combustion studies on tin tetra-alkyls are limited to those reported by Jones, Evans, Gulwell and Griffiths$^{(1)}$ on four compounds ($SnEt_4$, $SnPr_4$, $SnBu_4$ and $SnAm_4$), by Lippincott and Tobin$^{(2)}$ on $SnMe_4$, by Lautsch$^{(3)}$ and also by Baladin, Klabunorskü, Kozina and Ul'yanova$^{(4)}$ on $SnMe_4$ and $SnEt_4$, by Dillard, McNeill, Simmons and Yeldell$^{(5)}$ on seven compounds ($SnMe_4$, $SnMe_3Et$, $SnMe_2Et_2$, $SnMeEt_3$, $SnEt_4$, $SnEt_2Bu_2$ and $SnBu_4$), and by Rabinovich, Telnoi, Nikolaev and Razuvaev$^{(6)}$ on $SnEt_4$.

Jones *et al.*$^{(1)}$ gave no details of their experimental procedure, merely quoting the final heats of combustion obtained; it is now clear that their results were unreliable. Dillard, McNeill, Simmons and Yeldell$^{(5)}$ also give few details of the combustion experiments, but they have estimated the limits of error attached to their combustion results; there is, however, a lack of internal consistency in the results, and it is difficult to accept that the quoted error limits (which range from ±1 to ±5 kcal/mole) are realistic in all cases. Lippincott and Tobin$^{(2)}$ measured the heat of combustion of $SnMe_4$, and observed that the metal on occasions does not burn completely to form SnO_2, and that the oxide product formed in the crucible is blackened by traces of unburnt tin. Because of this difficulty, the results of individual combustion experiments showed a considerable scatter, and their recommended value for the standard heat of combustion, ΔH_c^o, was stated to be uncertain within limits of ±10 kcal/mole.

The combustion studies by Lautsch(3), by Baladin et al.(4), and by Rabinovich et al.(6), on $SnMe_4$ and $SnEt_4$, appear to have given more consistent results, and an accuracy within limits of ±3 - ±4 kcal/mole is claimed by these authors. The ΔH_c^o values (kcal/mole) for tin tetra-alkyls in the liquid state obtained by previous investigators are listed below, for comparison among themselves, and with the results reported here:-

Compound	I	II	III	IV	V	VI	VII
$SnMe_4$	-	903.5	906.0	905.7	934	-	912.4
$SnMe_3Et$	-	-	-	-	1034	-	1071.2
$SnMe_2Et_2$	-	-	-	-	1221	-	-
$SnMeEt_3$	-	-	-	-	1358	-	-
$SnEt_4$	1521	-	1548.0	1545.9	1547	1551	1551.5
$SnPr_4$	2163	-	-	-	-	-	-
$SnEt_2Bu_2$	-	-	-	-	2170	-	-
$SnBu_4$	2773	-	-	-	2816	-	-
$SnAm_4$	3384	-	-	-	-	-	-

Columns I - VI correspond to refs.(1) - (6).

Column VII - this research.

The main difficulty in bomb combustion studies on tin alkyls - and, indeed on organometallic compounds in general - is in ensuring the complete combustion of the compound, or, failing this, in making proper corrections for incomplete combustion when this occurs. The development of the rotating bomb calorimeter offers the best solution to problems of this type(7), but it should be possible to obtain satisfactory results by use of the conventional bomb calorimeter provided the following points are established:-

(i) The sample of metal alkyl used for combustion experiments is pure;

(ii) the mass of carbon dioxide produced on combustion corresponds to that calculated from the mass of sample introduced into the calorimeter;

(iii) the metal oxide formed on combustion is analysed for traces of unburnt metal, and proper correction made for this if necessary.

These requirements have largely been met in the present studies on $SnMe_4$ and $SnEt_4$: in the case of Me_3SnEt, the compound was not completely pure, and corrections were made assuming the impurity present to be Me_2SnEt_2. Satisfactory results were not obtained in preliminary experiments on $SnMe_4$, in which the bomb was charged with oxygen at the normal starting pressure of 30 atm.

On increasing this to 40 atm., combustion appeared to proceed more nearly to completion, only small traces of unburnt tin being found admixed with the metal oxide in the crucible after combustion.

2. Experimental Details

(i) Preparation and Purification of Compounds.

Tetramethyl tin was prepared by the method described by Edgell and Ward(8). The crude product was fractionated using a 6 ft. column packed with 'Knitmesh Multifil'; the fraction b.p. 77°C at 760 mm/Hg was retained. The gas chromatogram of this indicated the presence of a low boiling impurity, which was subsequently removed by fractional collection using a large-scale gas-phase chromatograph (12 ft. column, 4 cm. diameter, stationary phase of silicone oil on crushed firebrick). The purity of the final sample was measured at 99.94 mole % by use of the melting-point calorimeter described by Brooks and Pilcher(9).

Tetraethyl tin was prepared as described by Luijten and van der Kerk(10), from the reaction of ethyl magnesium bromide and stannic chloride. The crude product was treated with dry ammonia to remove traces of triethyl tin halides. This product was then fractionated under reduced pressure, and the sample b.p. 94.5°C at 28.5 mm/Hg retained. This was re-distilled from CaH_2 in vacuo : the chromatogram (Pye Argon chromatograph, polyester column at 100°C) showed a single peak, and no discernable impurity peaks. An attempt to measure the purity of the compound in the melting-point calorimeter failed to give a reliable result, presumably because of transitions between the various polymorphic crystalline forms(11).

Trimethylethyl tin was prepared by reacting trimethyl tin bromide (obtained by direct bromination of tetramethyl tin, as described by Kraus and Sessions(12)) with excess ethyl magnesium bromide. The crude product (b.p. 104 - 106°C) was diluted with ether and treated with dry NH_3 to remove traces of unreacted alkyl tin bromide. The ether was removed by distillation and the sample of product (b.p. 106 - 108°C) retained. This was passed through the large scale chromatograph (column temperature 96°C), and the fraction corresponding to the main peak collected : analysis of this on the Pye argon chromatograph showed the presence of a small amount of a high boiling impurity. The main sample was re-passed through the large-scale chromatograph, and the principal fraction dried over CaH_2, and redistilled in vacuo. However, the combustion results indicated that this sample was not pure, and contained a slight amount of an impurity with higher carbon content than Me_3SnEt. Since it is known that the bromination of $SnMe_4$ yields $SnMe_3Br$ contaminated with a little $SnMe_2Br_2$, it seems likely that the impurity involved was Me_2SnEt_2.

(ii) Calorimeter and Combustion Procedure.

The bomb calorimeter, similar in design to that described by Prosen and Rossini(13), was manufactured by Messrs. Baskerville and Lindsay, Manchester. The isothermal jacket, of the Dickinson(14) type was maintained at 28.000°C, the regulator being the 'Thermodyne' A.C. resistance bridge manufactured by Hallikainen Instruments. The temperature of the calorimeter was measured by a platinum resistance thermometer (Leeds Northrup Co.) and Smith's difference bridge (Cambridge Instrument Co.). The calorimeter was calibrated by burning samples of thermochemical standard benzoic acid provided by the National Bureau of Standards, Washington, D.C., and by B.D.H. Ltd.,

In the combustion experiments on tin alkyls, the bomb was charged with oxygen to an initial pressure of 40 atm., and the samples were fired at or near to 25°C. The liquid alkyls were contained in sealed polyester bags ('Melinex', 0.001" thickness) made as described by Good and Scott(15), and supported in a silica crucible[*]. The samples were fired electrically, by fusing a thin platinum wire which set fire to a cotton thread attached to the neck of the polyester container. The ensuing temperature rise of the calorimeter was normally of the order 3°C.

---

[*] This was replaced in some experiments by a silica crucible coated with a layer of stannic oxide. This made no significant difference to the measured heats of combustion, indicating that reaction between SnO_2 and the silica crucible is not a serious complication.

After each combustion experiment, the bomb-gases were analysed for carbon dioxide(13), and the bomb-washings for nitric acid. Analysis showed that no significant amount of nitric acid is retained (as nitrates of tin) in the crucible. The SnO_2 formed in the crucible usually contained a small amount of unburnt tin : this was estimated by weighing the crucible and contents on removal from the bomb (after carefully drying the crucible), igniting in a strong blowlamp flame, and re-weighing crucible and contents. Separate tests on made-up mixtures of SnO_2 with small amounts of powdered Sn metal showed that this procedure gives a reasonably accurate measure of the amount of free tin in the mixture.

Corrections for heat losses from the calorimeter were made by the method of Coops, Jessup and van Nes(16).

(iii) Units and Auxiliary Quantities.

The heats of combustion are given in joules, and derived heats of formation in thermochemical calories, defined by $1 \text{ cal.} \equiv 4.1840 \text{ abs.J.}$

The corrections for nitric acid formation (from traces of N_2 admixed with cylinder O_2) were based on 57.8 kJ/mole for the energy of formation of 0.1N nitric acid from N_2, O_2 and water.

The corrections for the ignition energy due to combustion of the cotton fuse were based on the value(16) of 16.24 kJ/g of cotton used.

The corrections for the energy of combustion of the 'Melinex' containers were determined from measurements of the heat of combustion of samples chosen from the stock roll of 'Melinex' film. From these, the mean value Δu_c^o = energy of combustion per gram. mass 'Melinex' = -22.868 ± 0.009 kJ was obtained. The analysis of bomb-gases from 'Melinex' combustions showed that 2.28352 g. CO_2 were formed per gram. mass of 'Melinex' burnt (i.e. 99.712% of the theoretical amount based on the ideal formula, $C_{10}H_8O_4$).

To correct weighings in air to mass *in vacuo*, the following density values (g/cm^3) at 20°C were accepted:-

$SnMe_4$	$SnEt_4$	$SnMe_3Et$	'Melinex'
1.314	1.187	1.243	1.38

The CO_2 produced on combustion was absorbed in Carbosorb-packed glass tubes which had been swept out with pure dry oxygen : to correct weighings to *in vacuo* values, the factor 1.00045 recommended by Rossini(17) was used.

Heats of formation, ΔH_f^o, were calculated from the standard heats of combustion, ΔH_c^o, assuming the following standard values:-

$$\Delta H_f^o\ (CO_2,\ \underline{g}.) = -94.052\ \text{kcal/mole}\ ^{(18)}$$

$$\Delta H_f^o\ (H_2O,\ \underline{liq}.) = -68.315\ \text{kcal/mole}\ ^{(18)}$$

$$\Delta H_f^o(SnO_2,\ \underline{c}.) = -138.81 \pm 0.8\ \text{kcal/mole}\ ^{(19)}$$

3. Results

The results of the combustion experiments are given in tables 1 - 3. The symbols have the following meanings:-

E_s = energy equivalent of the uncharged calorimeter system.

E_c = contribution to the total energy equivalent from the contents of the bomb after combustion.

ΔR_c = overall change in resistance of the Pt resistance thermometer, proportional to the corrected temperature rise.

q_i = energy of combustion of the cotton fuse.

q_{nit} = energy evolved by nitric acid formation.

q_M = energy evolved by combustion of 'Melinex' bag containing the sample.

q_{Sn} = energy correction for unburnt tin.

q_W = energy correction to standard states (i.e. Washburn corrections).

Δu_c^o = energy of combustion per gram substance introduced into the bomb.

Δu_c^o(corr.) = energy of combustion per gram substance burnt, as determined from the CO_2 recovery.

ΔU_c^o = energy of combustion per mole substance, determined from Δu_c^o(corr.)

In Table 3, Δu_c^o(corr.) is derived from Δu_c^o, correcting for an amount of Me_2SnEt_2 impurity determined from the deviation from 100% of the CO_2 recovered. The heat correction was made by assuming

$$\Delta U_c^o(Me_2SnEt_2) = \Delta U_c^o(Me_3SnEt) + \tfrac{1}{4}[\Delta U_c^o(SnEt_4) - \Delta U_c^o(SnMe_4)].$$

The error limits quoted for Δu_c^o, ΔU_c^o and ΔH_c^o are uncertainty intervals = 2 standard deviation of mean ; error limits attached to derived ΔH_f^o values include the uncertainty in the assumed value for $\Delta H_f^o(SnO_2$, c.).

TABLE 1 - Tetramethyl tin

$Sn(CH_3)_4$, M.W. = 178.830_2 (1961 values used)

E_S = 152.963 ± 0.017 kJ/ohm

q_W = -0.7 J

Expt. No.	1	2	3	4
$SnMe_4$ (mass, g.)	1.78447	1.82105	1.81569	1.79159
Melinex (mass, g.)	0.09173	0.07510	0.07545	0.08486
ΔR_c (ohms)	0.261706	0.264317	0.263654	0.261523
q_i (J.)	31.6	36.3	37.4	39.5
$q_{nit.}$ (J.)	6.3	10.9	3.9	2.7
q_M (J.)	2097.7	1717.4	1725.6	1940.8
q_{Sn} (J.)	27.1	18.4	15.0	38.3
E_c (kJ/ohm)	0.274	0.272	0.321	0.323
% CO_2 (recovered)	99.945	100.001	100.020	100.012
$-\Delta u_c^o$ (kJ/g)	21.292	21.283	21.294	21.291
$-\Delta u_c^o$ (corr.)	21.304	21.283	21.290	21.288

$-\Delta u_c^o$, mean value = 21.291 ± 0.010 kJ/g.

$-\Delta U_c^o$ = -910.01 ± 0.42 kcal/mole.

$-\Delta H_c^o$ = -912.38 ± 0.42 kcal/mole.

$-\Delta Hf^o$ ($SnMe_4$, <u>liq.</u>) = -12.53 ± 1.3 kcal/mole.

TABLE 2 - Tetraethyl tin

$Sn(C_2H_5)_4$; M.W. = 234.938_6

E_s = 152.963 ± 0.017 kJ/ohm

q_W = 5.8 J

Expt. No.	1	2	3	4
$SnEt_4$ (mass, g.)	1.42216	1.38472	1.42352	1.38507
Melinex (mass, g.)	0.07949	0.08286	0.08269	0.08284
ΔR_c (ohms)	0.267786	0.261550	0.268530	0.261554
q_i (J.)	34.3	35.1	35.7	40.3
$q_{nit.}$ (J.)	2.5	3.2	6.7	1.5
q_M (J.)	1817.8	1894.8	1891.0	1894.4
q_{Sn} (J.)	4.6	8.4	6.3	1.6
E_c (kJ/ohm)	0.327	0.320	0.328	0.321
% CO_2 (recovered)	100.012	99.941	99.988	99.869
$-\Delta u_c^o$ (kJ/g.)	27.559	27.558	27.559	27.545
$-\Delta u_c^o$ (corr.)	27.556	27.574	27.562	27.581

cont.

TABLE 2 (continued)

5	6	7
1.40130	1.37326	1.42237
0.07971	0.07870	0.07019
0.263763	0.258655	0.266267
42.1	35.8	38.9
1.5	3.0	2.0
1822.8	1799.7	1605.1
15.7	9.1	8.6
0.324	0.318	0.325
99.865	99.933	99.853
27.528	27.534	27.540
27.565	27.552	27.581

$-\Delta u_c^o$, mean value = 27.567 ± 0.010 kJ/g.

ΔU_c^o = -1547.93 ± 0.56 kcal/mole.

ΔH_c^o = -1551.48 ± 0.56 kcal/mole.

ΔH_f^o ($SnEt_4$, liq.) = -22.90 ± 1.4 kcal/mole.

TABLE 3 - Trimethyl ethyl tin

$Sn(CH_3)_3(C_2H_5)$; M.W. = 192.857_3

E_s = 152.963 ± 0.017 kJ/ohm

q_W = 1.8 J.

Expt. No.	1	2	3	4	5
$SnMe_3Et$ (mass, g.)	1.69536	1.66083	1.65339	1.64506	1.66348
Melinex (mass, g.)	0.07110	0.08927	0.08242	0.08058	0.07701
ΔR_c (ohms)	0.267614	0.265140	0.263048	0.261380	0.263737
q_i (J.)	41.9	38.3	39.5	34.7	35.9
$q_{nit.}$ (J.)	2.3	3.0	2.3	1.6	14.5
q_M (J.)	1625.9	2041.4	1884.8	1842.7	1761.1
q_{Sn} (J.)	16.3	17.8	10.8	17.5	9.4
E_c (kJ/ohm)	0.317	0.318	0.320	0.326	0.327
% CO_2 (recovered)	100.234	100.183	100.374	100.388	100.297
$-\Delta u_c^o$ (kJ/g. substance)	23.219	23.226	23.227	23.223	23.219
$-\Delta u_c^o$ (corr.)	23.186	23.200	23.175	23.169	23.178

$-\Delta u_c^o$ (corr.), mean value = 23.182 ± 0.012 kJ/g.

ΔU_c^o = -1068.55 ± 0.55 kcal/mole.

ΔH_c^o = -1071.22 ± 0.55 kcal/mole.

ΔH_f^o ($SnMe_3Et$, <u>liq.</u>) = -16.06 ± 1.4 kcal/mole.

4. Discussion

The heats of formation of liquid tetramethyl lead and tetraethyl lead have recently been obtained from combustion measurements in a rotating bomb calorimeter by Good, Scott, Lacina and McCullough(20) and by Scott, Good and Waddington(21). The standard heats of formation are compared below with those now reported for the corresponding tin alkyls:-

	$SnMe_4$	$SnEt_4$	$PbMe_4$	$PbEt_4$
ΔH_f^o (liq.) (kcal/mole)	-12.5±1.3	-22.9±1.4	23.5±0.3	12.7±0.4

It is of interest to note that the difference, $\Delta H_f^o[MMe_4] - \Delta H_f^o[MEt_4]$, is virtually the same for M = Sn (difference = 10.4 ± 1.9 kcal/mole) as for M = Pb (difference = 10.8 ± 0.5 kcal/mole).

Bullard and Haussman(22) have given vapour pressure data over a range of temperature for $SnMe_4$ and $SnMe_3Et$, from which the heats of vaporisation at 25°C may be derived, viz:- $\Delta H_{vap}(SnMe_4)$ = 7.9 kcal/mole, and $\Delta H_{vap}(SnMe_3Et)$ = 8.85 kcal/mole: these values should be reliable within limits of <u>ca</u>. ± 0.3 kcal/mole. Vapour pressure data are scanty for $SnEt_4$, and our estimated value $\Delta H_{vap} \sim 10.9$ kcal/mole may be in error by <u>ca</u>. ± 0.6 kcal/mole.

On combining these ΔH_{vap} values with the measured ΔH_f^o(<u>liq.</u>) values given above, the standard heats of formation of the <u>gaseous</u> compounds are obtained:-

	ΔH_f^o(g.), kcal/mole
$SnMe_4$	-4.6 ± 1.6
$SnMe_3Et$	-7.2 ± 1.7
$SnEt_4$	-12.0 ± 2.0

The latter, in conjunction with the recommended values $\Delta H_f^o(Sn,\underline{g}.) = 72 \pm 2$ kcal/mole(23), $\Delta H_f^o(CH_3,\underline{g}.) = 32.5 \pm 1$ kcal/mole(24) and $\Delta H_f^o(C_2H_5,\underline{g}) = 25.5 \pm 2$ kcal/mole(24) enable the heats of the following dissociation processes to be evaluated (in kcal/mole) :-

$SnMe_4(g) \rightarrow Sn(g) + 4CH_3(g)$; $\Delta H = 206.6 \pm 7.6$

$SnMe_3Et(g) \rightarrow Sn(g) + 3CH_3(g) + C_2H_5(g)$; $\Delta H = 202.2 \pm 8.7$

$SnEt_4(g) \rightarrow Sn(g) + 4C_2H_5(g)$; $\Delta H = 186.0 \pm 12$

Thus, the <u>mean</u> bond dissociation energy in tetramethyl tin has the value $\bar{D}(Sn - CH_3) = 51.65 \pm 2$ kcal/mole ; in tetraethyl tin, the corresponding mean energy $\bar{D}(Sn - C_2H_5) = 46.5 \pm 3$ kcal/mole. These $\bar{D}$ values are appreciably larger than the $\bar{D}$ values in the corresponding tetra alkyls of lead, for which $\bar{D}(Pb - CH_3) = 36.05 \pm 1.2$ kcal/mole and $\bar{D}(Pb - C_2H_5) = 31.5 \pm 2.5$ kcal/mole, and reflect the greater thermal stability of tin alkyls relative to those of lead.

Pedley, Skinner and Chernick(25) measured the heats of bromination of tetramethyl tin and of hexamethyl distannane, obtaining:-

$$\text{(i)}\quad \text{SnMe}_4(\underline{\text{liq.}}) + \text{Br}_2(\underline{\text{g.}}) \rightarrow \text{Me}_3\text{SnBr}(\underline{\text{liq.}}) + \text{MeBr}(\underline{\text{g.}})$$

$$\Delta H = -48.3 \pm 0.7 \text{ kcal/mole}$$

and

$$\text{(ii)}\quad \text{Sn}_2\text{Me}_6(\underline{\text{liq.}}) + \text{Br}_2(\underline{\text{liq.}}) \rightarrow 2\text{Me}_3\text{SnBr}(\underline{\text{liq.}})$$

$$\Delta H = -70.24 \pm 0.5 \text{ kcal/mole.}$$

On making use of the present value for $\Delta H_f^o(\text{SnMe}_4, \underline{\text{liq.}})$, and the recommended values $\Delta H_f^o(\text{Br}_2, \underline{\text{g.}}) = 7.39 - 0.03$ kcal/mole(26), $\Delta H_f^o(\text{MeBr}, \underline{\text{g.}}) = -9.6 - 0.5$ kcal/mole(24), the values

$$\Delta H_f^o(\text{Me}_3\text{SnBr}, \underline{\text{liq.}}) = \pm 43.8_4 \pm 1.6 \text{ kcal/mole}$$

$$\Delta H_f^o(\text{Sn}_2\text{Me}_6, \underline{\text{liq.}}) = \pm 17.4_4 \pm 3.3 \text{ kcal/mole}$$

are derived from (i) and (ii). Combining the latter value with the measured heat of iodination of hexamethyl distannane(25),

$$\text{(iii)}\quad \text{Sn}_2\text{Me}_6(\underline{\text{liq.}}) + \text{I}_2(\underline{\text{c.}}) \rightarrow 2\text{Me}_3\text{SnI}(\underline{\text{liq.}})$$

$$\Delta H = -44.02 \pm 0.7 \text{ kcal/mole}$$

we may also derive :

$$\Delta H_f^o(\text{Me}_3\text{SnI}, \underline{\text{liq.}}) = -30.7_3 \pm 1.7 \text{ kcal/mole.}$$

Measurements have also been reported by Pedley and Skinner(27) for the heats of bromination of trimethyl phenyl tin, trimethyl benzyl tin, and trimethyl vinyl tin : these results may now be re-evaluated, using the present value for $\Delta H_f^o(Me_3SnBr,$ __liq.__$)$, and the recommended values(27,24) $\Delta H_f^o(PhBr,$ __liq.__$) = 13 \pm 2$ kcal/mole, $\Delta H_f^o(PhCH_2Br,$ __liq.__$) = 5 \pm 3$ kcal/mole, and $\Delta H_f^o(CH_2{=}CHBr,$ __g.__$) = 18.7 \pm 0.5$ kcal/mole, to give:-

$$\Delta H_f^o(Me_3SnPh, \underline{liq.}) = 13.6 \pm 2.5 \text{ kcal/mole}$$

$$\Delta H_f^o(Me_3SnCH_2Ph, \underline{liq.}) = 7.9 \pm 3.4 \text{ kcal/mole}$$

and $$\Delta H_f^o(Me_3SnCH{=}CH_2, \underline{liq.}) = 13.2 \pm 1.7 \text{ kcal/mole}$$

By subtracting the ΔH_f^o value for trimethyl vinyl tin from that for trimethyl ethyl tin, we may derive the heat of hydrogenation of the former, viz:-

$$Me_3SnCH{=}CH_2(\underline{liq.}) + H_2(\underline{g.}) \rightarrow Me_3SnEt(\underline{liq.})$$

$$\Delta H = -29.3 \pm 2.2 \text{ kcal/mole.}$$

This value agrees very well with the measured heat of hydrogenation of the analogous hydrocarbon, 33-dimethylbut-1-ene ($\Delta H = -30.34$ kcal/mole), in the vapour phase(28), and may be regarded as evidence of internal consistency in the present results.

The bond dissociation energy, D(Me_3Sn-CH_3), of the process $Sn(CH_3)_4 \rightarrow Sn(CH_3)_3 + CH_3$, has not been measured, but, as pointed out by Pedley et al.(25), is probably of similar magnitude to the mean bond dissociation in $SnMe_4$, $\bar{D}(Sn-CH_3)$ = 51.65 (±2) kcal/mole. If we equate the bond dissociation energy D(Me_3Sn-CH_3) to the mean $\bar{D}$ value, the value $\Delta H_f^o(Me_3Sn, g.)$ = 14.55 (±2) kcal/mole is obtained: this has been used to derive the dissociation energies, D(Me_3Sn-R), listed below:-

Compound	ΔH_{vap} (estimated)	$\Delta H_f^o(g.)$ (kcal/mole)	Bond dissociation energy (kcal/mole)
Me_3SnBr	11.4	-32.4 ± 2	Me_3Sn-Br = 73.7 ± 3
Me_3SnI	11.5	-19.2 ± 2	Me_3Sn-I = 59.3 ± 3
Me_3SnPh	12.5	26.1 ± 3	Me_3Sn-Ph = 58.5 ± 5
Me_3SnBz	13.5	21.4 ± 4	Me_3Sn-Bz = 33.2 ± 6
Me_3SnVn	8.6	21.8 ± 2	Me_3Sn-Vn = 58.2 ± 4
$Me_3SnSnMe_3$	12.0	- 5.4 ± 4	$Me_3Sn-SnMe_3$ = 34.5 ± 5

(Bz = benzyl, Vn = vinyl)

Values for $\Delta H_f^o(Ph)$ and $\Delta H_f^o(Bz)$ recommended by Skinner(24), and the value(29) $\Delta H_f^o(Vn)$ = 65.4 ± 3 kcal/mole were accepted.

The value for the Sn-Sn dissociation energy in $Me_3Sn-SnMe_3$ compares well with bond energy term value of 36 ± 1 kcal in grey tin. We may also note that the Sn-C dissociation energies in phenyl-Sn and vinyl-Sn compounds are enhanced relative to $\bar{D}(Sn-CH_3)$: the same trends are apparent in C-C bond dissociation energies(30).

Abstract

The heats of combustion at 25°C (under 40 atm. oxygen pressure) of liquid tetramethyl tin, tetraethyl tin, and trimethylethyl tin, have been measured in a bomb calorimeter. Values for the standard heats of formation were derived from the combustion results:-

$$\Delta H_f^o(\mathrm{SnMe_4},\ \underline{\mathrm{liq.}}) = -12.5_3 \pm 1.3 \text{ kcal/mole}$$

$$\Delta H_f^o(\mathrm{SnMe_3Et},\underline{\mathrm{liq.}}) = -16.0_6 \pm 1.4 \text{ kcal/mole}$$

$$\Delta H_f^o(\mathrm{SnEt_4},\ \underline{\mathrm{liq.}}) = -22.9_0 \pm 1.4 \text{ kcal/mole.}$$

By combining these data with previously reported heats of bromination of various alkyl tin compounds, the heats of formation of trimethyl tin bromide, trimethyl tin iodide, trimethylphenyl tin, trimethylbenzyl tin, trimethylvinyl tin and hexamethyl distannane were obtained.

References

1. Jones, Evans, Gulwell and Griffiths, J.Chem.Soc., 1935, 39.
2. Lippincott and Tobin, J.Amer.Chem.Soc., 1953, 75, 4141.
3. Lautsch, Chem.Tech. (Berlin), 1958, 10, 419.
4. Baladin, Klabunovskii, Kozina and Ul'yanova, Izvest.Akad.Nauk SSSR, 1957,
5. Dillard, McNeill, Simmons and Yeldell, J.Amer.Chem.Soc., 1958, 80, 3607.
6. Rabinovich, Telnoi, Nicklaev and Razuvaev, Doklady Akad.Nauk SSSR, 1961, 138, 852.
7. Good and Scott, Chap.4 in "Experimental Thermochemistry", Vol.2, edited by H.A. Skinner, Interscience-Wiley, New York,1962.
8. Edgell and Ward, J.Amer.Chem.Soc., 1954, 76, 1169.
9. Brooks and Pilcher, J.Chem.Soc. , 1959, 1535.
10. Luijten and van der Kerk, 'Organotin Chemistry', p.95, Tin Research Institute, Greenford, Middlesex, 1955.
11. Staveley, Paget, Goalby and Warren, J.Chem.Soc., 1950, 2290.
12. Kraus and Sessions, J.Amer.Chem.Soc., 1925, 47, 2361.
13. Prosen and Rossini, J.Research Natl.Bur.Standards, 1941, 27, 289.
14. Dickinson, Bull.Bur.Standards, 1914, 11, 188.
15. Good and Scott, 'Experimental Thermochemistry', Vol.2, Chap.2, Interscience, New York,1962.
16. Coops, Jessup and van Nes, 'Experimental Thermochemistry', Vol.I, Chap.3, Interscience, New York, 1956.
17. Rossini, 'Experimental Thermochemistry', Vol.I, Chap.4, Interscience, New York, 1956.

18. National Bureau of Standards, Washington, D.C., Circular 500, 1952.

19. Humphrey and O'Brien, J.Amer.Chem.Soc., 1953, 75, 2805.

20. Good, Scott, Lacina and McCullough, J.Phys.Chem., 1959, 63, 1139.

21. Scott, Good and Washington, J.Phys.Chem., 1956, 60, 1090.

22. Bullard and Haussmann, J.Phys.Chem, 1930, 34, 741.

23. Brewer, 'Electronic Structure and Alloy Chemistry of Transition Elements', A.I.M.E. Monograph Series, Interscience, New York, 1962.

24. Skinner, Roy.Inst.Chem, Lectures, Monographs and Reports, No.3, 1958.

25. Pedley, Skinner and Chernick, Trans.Faraday Soc., 1957, 53, 1612.

26. JANAF Thermochemical Tables, edited by D.R. Stull, Dow Chemical Co., Midland, Mich., 1960-62.

27. Pedley and Skinner, Trans.Faraday Soc., 1959, 55, 544.

28. Dolliver, Gresham, Kistiakowsky and Vaughan, J.Amer.Chem.Soc., 1937, 59, 851.

29. Harrison and Lossing, J.Amer.Chem.Soc., 1960, 82, 519.

30. Roberts and Skinner, Trans.Faraday Soc., 1949, 45, 339.