# The enthalpies of formation of 1,1-diphenylstannacyclopentane and 1,1-diphenylstannacyclohexane and some associated tin-carbon bond-enthalpy terms

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The two compounds  $(C_6H_5)_2Sn(CH_2)_4$  and  $(C_6H_5)_2Sn(CH_2)_5$  have been burnt in an aneroid combustion bomb and their vapour pressures measured by an effusion method.

$$\begin{split} \Delta_{f} H^{\circ}_{\mathfrak{m}} \{ (C_{6}H_{5})_{2} \text{Sn}(\text{CH}_{2})_{4}, \text{ cr} \} &= (195.0 \pm 5.2) \text{ kJ} \cdot \text{mol}^{-1}; \\ \Delta_{sub} H_{\mathfrak{m}} \{ (C_{6}H_{5})_{2} \text{Sn}(\text{CH}_{2})_{4} \} &= (106.8 \pm 5.5) \text{ kJ} \cdot \text{mol}^{-1}; \\ \Delta_{f} H^{\circ}_{\mathfrak{m}} \{ (C_{6}H_{5})_{2} \text{Sn}(\text{CH}_{2})_{5}, 1 \} &= (214.0 \pm 6.1) \text{ kJ} \cdot \text{mol}^{-1}; \\ \Delta_{vap} H_{\mathfrak{m}} \{ (C_{6}H_{5})_{2} \text{Sn}(\text{CH}_{2})_{5} \} &= (75.0 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}. \end{split}$$

The gas-phase molar enthalpies of formation have been used to obtain C-Sn bond-enthalpy terms and give information about strain in the ring systems.

#### 1. Introduction

The standard molar enthalpies of formation of

 $(C_6H_5)_2Sn$  and  $(C_6H_5)_2Sn$ 

in the gas phase have been obtained from combustion calorimetry and Knudsen effusion. The results have been used to investigate whether or not strain is present in the ring systems.

### 2. Experimental

1,1-Diphenylstannacyclopentane was prepared<sup>(1, 2)</sup> by adding 18.4 g of 1,4-dibromobutane in 250 cm<sup>3</sup> of dry ether to magnesium turnings to produce the di-Grignard reagent; 24.1 g of diphenyl tin dichloride in 500 cm<sup>3</sup> of dry ether was then added slowly to the Grignard reagent at room temperature and the mixture was refluxed for 3 h. The mixture was cooled and hydrolysed by pouring it into ice-cold 1 mol  $\cdot$  dm<sup>-3</sup> HCl. The organic layer was decanted, washed with a 10 mass per cent solution of KF, filtered, decanted a second time, and dried over magnesium

Sample	1	$10^2 x$
	d.s.c.	h.p.l.c.
1	99.5	>99
2	99.3	99.0+0.3
3	99.6	$99.3 \pm 0.3$
4	99.7	> 99.7
5	99.7	

TABLE 1. Results of mole-percentage  $10^2x$  purity measurements on 1,1-diphenylstannacyclopentane

sulphate. The solvent was removed and the residual oil was distilled; the fraction boiling at 401 to 403 K at 13 Pa was collected. This was a colourless oil which solidified in a refrigerator. The sample was recrystallized twice from pentane and showed a sharp melting temperature at 311 K. Analysis gave carbon and hydrogen mass percentages of 58.35 and 5.35 compared with the theoretical values of 58.43 and 5.52. The purity of part of the sample was estimated by d.s.c. and/or h.p.l.c. following each combustion experiment. The results are shown in table 1. The sample was recrystallized prior to combustion 3 and a new sample was prepared for combustions 4 and 5.

The preparation of 1,1-diphenylstannacyclohexane followed a similar course. The residual oil was distilled and the fraction boiling at 395 to 398 K at 13 Pa was collected and stored under nitrogen in a refrigerator. After standing for several days the colourless oil became slightly turbid, which might have been due to dimer formation; consequently before each combustion a sample was prepared by using a Kugelrohr distillation apparatus. The purity of each sample was checked by h.p.l.c. and by carbon and hydrogen analysis; the mean mass percentages were 59.49 and 5.88 compared with the theoretical values of 59.52 and 5.88. The results are shown in table 2.

The vacuum-jacketed aneroid combustion calorimeter and its use as a static instrument for the combustion of organo-tin compounds have been described previously.<sup>(3)</sup>

## 3. Results

In table 3 which refers to the combustion of 1,1-diphenylstannacyclopentane we have m, mass; M, molar mass;  $\rho$ , density;  $\Delta R$ , corrected resistance change;  $q_T$ ,

TABLE 2. Results of mass-percentage  $10^2w$  and mole-percentage  $10^2x$  purity measurement on 1,1-diphenylstannacyclohexane

Sample	Elementa 10	h.p.l.c. $10^2 x$		
	59.25	5.80	99.4+0.5	
2	59.40	5.95	$99.4 \pm 0.5$	
3	59.70	5.85	$99.3 \pm 0.5$	
4	59.45	5.90	99.4+0.5	
5	59.65	5.90	$99.4 \pm 0.5$	

TABLE 3. Results of measurements of the molar energy of combustion of 1,1-diphenylstannacyclopentane:  $M = 329.012 \text{ g} \cdot \text{mol}^{-1}$ ;  $\rho = 1.6 \text{ g} \cdot \text{cm}^{-3}$ 

No.	m(cpd)/g	$\Delta R/\Omega$	q <sub>T</sub> /kJ	$q_{\rm m}/{ m kJ}$	q₁/kJ	$q_{n}/\mathrm{kJ}$	q <sub>i</sub> /kJ	q <sub>c</sub> /kJ	$q_{ m w}/{ m kJ}$	$-\Delta_{\rm c} u^{\circ}/({\rm kJ}\cdot{\rm g}^{-1})^a$
1	0.185590	0.26815	5.9682	0.5192	0.0418	0.0005	0.0227	0.0055	0.0030	29.2683
2	0.168906	0.24587	5.4723	0.5248	0.0424	0.0002	0.0214	0.0202	0.0028	29.2689
3	0.173342	0.25042	5.5736	0.4829	0.0436	0.0002	0.0212	0.0121	0.0029	29.2907
4	0.174420	0.25178	5.6038	0.4844	0.0436	0.0005	0.0211	0.0088	0.0030	29.2524
5	0.166657	0.24316	5.4120	0.5278	0.0381	0.0004	0.0209	0.0156	0.0028	29.2781
								mean value:		29.2717

 $a^{-} - \Delta_{c} u^{\circ} = \{q_{T} - q_{n} - q_{f} - q_{m} + q_{c} + q_{i} - q_{w}\}/m(cpd).$  $-\Delta_{c} U_{m}^{\circ} = (9630.7 \pm 4.7) \text{ kJ} \text{ mol}^{-1}, \text{ where the uncertainty is twice the standard deviation of the }$ means and includes the uncertainties in the calibrations and the melinex combustions;  $-\Delta_{\rm c}H_{\rm m}^{\circ} = (9644.4 \pm 4.7) \text{ kJ} \cdot \text{mol}^{-1}; \ \Delta_{\rm f}H_{\rm m}^{\circ}({\rm C}_{16}{\rm H}_{18}{\rm Sn}, {\rm cr}) = (195.0 \pm 5.2) \text{ kJ} \cdot {\rm mol}^{-1}.$ 

total energy change;  $q_n$ , energy correction for nitric-acid formation;  $q_f$ , energy correction for the cotton fuse;  $q_{\rm m}$ , energy connection for the combustion of Melinex;  $q_{\rm c}$ , energy correction for incomplete combustion;  $q_{\rm i}$ , correction involved in reducing the combustion process to 298.15 K;  $q_w$ , the Washburn correction. Table 4 contains the corresponding values for 1,1-diphenylstannacyclohexane. In obtaining the  $\Delta_f H_m^\circ$  values the following were used:  $\Delta_f H_m^\circ(CO_2, g)$  $-(393.51\pm0.13) \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(4)</sup>  $\Delta_{f} H^{\circ}_{m}(\text{H}_{2}\text{O}, \textbf{l}) = -(285.83\pm0.04) \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(4)</sup> and  $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm SnO}_2,{\rm cr}) = -(580.78 \pm 3.30) \,{\rm kJ} \cdot {\rm mol}^{-1}.^{(5)}$ 

The molar enthalpy of fusion of the cyclopentane compound was found by using d.s.c. to be  $(11.56\pm0.08)$  kJ·mol<sup>-1</sup> and the molar enthalpy of vaporization was found to be  $(92.8\pm5.5)$  kJ·mol<sup>-1</sup>, using a combined mass-loss torsional-recoil effusion method,<sup>(6)</sup> in the temperature range 303 to 327 K. An attempt to measure the sublimation enthalpy directly by studying the effusion at temperatures below the melting temperature was not successful; the results were too erratic to be of value.

The effusion method was also used to measure the molar enthalpy of vaporization of the stannacyclohexane in the temperature range 295 to 340 K. The value found was (73.2 + 1.5) kJ · mol<sup>-1</sup>.

The heat capacities of the solid and liquid phases were measured by d.s.c. and those of the vapours were estimated by using the Benson<sup>(7)</sup> group parameters. The

TABLE 4. Results of measurements of the energy of combustion of 1,1-diphenylstannacyclohexane:  $M = 343.039 \text{ g} \cdot \text{mol}^{-1}; \rho = 1.6 \text{ g} \cdot \text{cm}^{-3}$ 

No.	m(cpd)/g	$\Delta R/\Omega$	q <sub>T</sub> ∕kJ	$q_{\rm m}/{ m kJ}$	$q_{\rm f}/{ m kJ}$	q <sub>n</sub> /kJ	$q_{\rm i}/{ m kJ}$	q <sub>c</sub> /kJ	q <sub>₩</sub> /kJ	$-\Delta_{\rm c} u^{\circ}/({\rm kJ}\cdot{\rm g}^{-1})$
3	0.245054	0.3634	8.0934	0.6976	0.0417	0.0001	0.0290	0.0044	0.0040	30,1297
4	0.160568	0.24632	5.4824	0.6477	0.0384	0.0003	0.0213	0.0176	0.0028	30.0938
5	0.165972	0.25494	5.6742	0.6394	0.0577	0.0002	0.0219	0.0046	0.0029	30.1286
6	0.151863	0.23322	5.1908	0.6053	0.0398	0.0002	0.0205	0.0059	0.0027	30.0876
7	0.160723	0.24272	5.4021	0.5637	0.0334	0.0004	0.0211	0.0139	0.0027	30.0945
								me	an value:	30.1069

 $-\Delta_{\rm c} U_{\rm m}^{\circ} = (10327.8 \pm 6.3) \, \rm kJ \cdot mol^{-1}; \ -\Delta_{\rm c} H_{\rm m}^{\circ} = (10342.7 \pm 6.3) \, \rm kJ \cdot mol^{-1};$  $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm C}_{17}{\rm H}_{20}{\rm Sn},{\rm l}) = (214.0 \pm 6.8) \,\rm kJ \cdot mol^{-1}.$ 

molar enthalpy of sublimation of the cyclopentane compound and the molar enthalpy of vaporization of the cyclohexane compound, reduced to 298.15 K are  $(106.8\pm5.5)$  kJ·mol<sup>-1</sup> and  $(75.0\pm1.5)$  kJ·mol<sup>-1</sup>, respectively. Therefore, the standard molar enthalpies of formation in the gas phase are

$$\Delta_{f} H^{\circ}_{m} \{ (C_{6}H_{5})_{2} \operatorname{Sn}(CH_{2})_{4}, g \} = (301.8 \pm 7.5) \text{ kJ} \cdot \text{mol}^{-1}, \Delta_{f} H^{\circ}_{m} \{ (C_{6}H_{5})_{2} \operatorname{Sn}(CH_{2})_{5}, g \} = (289.0 \pm 6.3) \text{ kJ} \cdot \text{mol}^{-1}.$$

We have discussed previously<sup>(3, 8)</sup> self-consistent bond-enthalpy term schemes for some of the organo-compounds of tin. For straight-chain compounds  $E\{C(sp^3)-Sn\}$ = 202.9 kJ·mol<sup>-1</sup>, and it is of interest to see if this value is changed, because of strain, when the tin is part of a ring system.

The standard molar enthalpy of atomization of  $(C_6H_5)_2Sn(CH_2)_4$  is 15365.1 kJ·mol<sup>-1</sup> which may be represented by the contributions:

$$-2\Delta_{a}H_{m}^{\circ}(C_{6}H_{5}\cdot)+2E\{C(ar)-Sn\}+2E\{C(sp^{3})-Sn\}+3E\{C(sp^{3})-C\}$$
  
+8E{C(sp^{3})-H}- $\Delta$ (ring strain) = (10189.46+436.6+405.8  
+1072.95+3255.84) kJ \cdot mol^{-1}.

so that  $\Delta = -(4.4 \pm 5.2) \text{ kJ} \cdot \text{mol}^{-1}$ . The standard molar enthalpy of atomization of  $(C_6H_5)_2Sn(CH_2)_5$  is 16528.25 kJ·mol<sup>-1</sup> which may be represented by the contributions:

$$-2\Delta_{a}H_{m}^{\circ}(C_{6}H_{5}\cdot)+2E\{C(ar)-Sn\}+2E\{C(sp^{3})-Sn\}+4E\{C(sp^{3})-C\}$$
  
+10E{C(sp^{3}-H)}- $\Delta$ (ring strain) = (10189.46+436.6+405.8  
+1430.6+4069.8) kJ · mol<sup>-1</sup>.

so that  $\Delta = (3.8 \pm 6.1) \text{ kJ} \cdot \text{mol}^{-1}$ . Thus, within the limits of experimental error, there is no evidence of strain in these ring compounds. This is not unexpected in the tin cyclohexane but, in view of the fact that the usually accepted value for strain in five-membered carbon rings is  $26.4 \text{ kJ} \cdot \text{mol}^{-1}$ , it is surprising that this appears to be true also in the cyclopentane system. The apparent absence of strain may be due to the fact that the C(sp<sup>3</sup>)-Sn link is considerably longer (0.218 nm) than the C(sp<sup>3</sup>)-C(sp<sup>3</sup>) one (0.154 mm).

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