Bonding Studies of Compounds of Boron and the Group IV Elements. Part VIII.[1] Heats of Hydrolysis and Bond Energies for Some Trimethylmetalyl Derivatives $Me_3M–X$ (M = Si, Ge, and Sn)

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The heats of hydrolysis, in aqueous 1 M-hydrochloric acid, of one silicon, five germanium, and eight tin(IV) compounds of type $(Me_3M)_nX$ (where M = Si, Ge, or Sn, n = 1—3, and X is a univalent ligand in which the donor atom adjacent to M is N, O, S, Cl, Br, or I) to give $(Me_3Si)_2O$, $(Me_3Ge)_2O$, and $(Me_3SnOH)_2$ have been measured. From these, standard heats of formation have been calculated as follows: ΔH_f° ($Me_3Si{\cdot}OEt$), l = −126·4 ± 0·7; ΔH_f° [$(Me_3Ge)_2O$], l = −136·0 ± 4·0; ΔH_f° (Me_3GeCl), l = −71·6 ± 2·1; ΔH_f° (Me_3GeBr), l = −62·1 ± 2·1; ΔH_f° ($Me_3Ge{\cdot}OEt$), l = −95·8 ± 2·2; ΔH_f° ($Me_3Ge{\cdot}SBu^n$), l = −64·7 ± 2·1; ΔH_f° ($Me_3Ge{\cdot}NMe_2$), l = −37·1 ± 2·2; ΔH_f° (Me_3SnCl), c = −58·4 ± 1·2; ΔH_f° (Me_3SnBr), c = −48·8 ± 1·3; ΔH_f° (Me_3SnI), l = −31·2 ± 1·1; ΔH_f° (Me_3SnOH), c = −90·8 ± 1·2; ΔH_f° ($Me_3Sn{\cdot}OEt$), l = −73·1 ± 1·5; ΔH_f° ($Me_3Sn{\cdot}SBu^n$), l = −47·1 ± 1·6; ΔH_f° ($Me_3Sn{\cdot}NMe_2$), l = −13·3 ± 1·4; ΔH_f° [$(Me_3Sn)_2NMe$], l = −31·5 ± 2·5; ΔH_f° [$(Me_3Sn)_3N$], c = −29·2 ± 3·6 kcal mol^{-1}. Gas-phase enthalpies of formation of these compounds and thermochemical bond energy terms E(M–X) have been calculated. Group trends show that, for constant X, $E(C–X) < E(Si–X) > E(Ge–X) > E(Sn–X)$, whereas $E(C–Y) > E(Si–Y)$ (Y = H or Me). Another conclusion is that the 'softness' (in terms of ΔH of reactions) of the acids Me_3M^+ increase in the order C < Si < Ge < Sn; several chemical reaction types are examined in this light.

In Part I we described calorimetric experiments which furnished heats of hydrolysis of some compounds of general formula $(Me_3Si)_nX$, namely those in which $n = 1$, with X = Cl, Br, OH, OBu^n, NHMe, and NMe_2; $n = 2$, with X = NH or NMe; and $n = 3$, with X = N.[2] We now report extensions of this work to $n = 1$, with X = OEt, and $n = 2$, with X = O, as well as to some germanium and tin(IV) analogues of these silicon compounds. The two papers should in many ways be seen as a single whole. The work is also related to (i) mass spectrometric studies on the compounds Me_4M^1 and $Me_3M^1–M^2Me_3$ (M^1 and M^2 = C, Si, Ge, Sn, and Pb), which yielded gas-phase enthalpies of formation [ΔH_f° (g)] of these two classes of compound and of radicals and ions derived from them;[3] (ii) rotating bomb calorimetric studies on Et_4Si and Me_6Si_2;[1] and (iii) other thermochemical data on Group IV compounds.[4,5]

The compounds studied are $(Me_3M)_nX$, where M = Si, Ge, or Sn, and X is a univalent ligand in which the atom adjacent to M has one or more formally non-bonding electron pairs (*i.e.*, N, O, S, Hal). Spectroscopy (^1H n.m.r.) revealed that, under calorimetric conditions, acid hydrolysis was rapid and quantitative to afford $(Me_3Si)_2O$, $(Me_3Ge)_2O$, and $(Me_3Sn{\cdot}OH)_2$, respectively. For simplicity, thermochemical data for $(Me_3SnOH)_2$ refer to the monomer formula: strictly, they therefore relate to g.f.w.$^{-1}$, (gram-formula weight)$^{-1}$, rather than

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[1] Part VII, B. S. Iseard, J. B. Pedley, and J. A. Treverton, *J. Chem. Soc.* (*A*), 1971, 3095.

[2] Part I, J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. A. Treverton, *J. Chem. Soc.* (*A*), 1967, 1980.

[3] Part VI, M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, *J. Organometallic Chem.*, 1971, **29**, 195.

[4] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London–New York, 1970.

[5] 'Selected Values of Chemical Thermodynamic Properties', Nat. Bur. Stand. Tech. Note 270-3, U.S. Government Printing Office, Washington D.C., 1968.

mol^{-1}. The compounds Me_3SiF and Me_3SnF were also examined: the silicon compound (b.p. 17 °C) proved inacceptably volatile for use in the calorimeter, while the tin fluoride did not react. In the hope of obtaining $\bar{E}$(Si–Hg), the reaction of $(Me_3Si)_2Hg$ with oxygen in benzene was investigated but was found to be non-stoicheiometric.

From subsidiary data,[4,5] heats of hydrolysis thus provide standard enthalpies of formation ΔH_f° (c or l) which, with literature or calculated heats of vaporisation ΔH_{vap}, lead to ΔH_f° (g). From ΔH_f° (g), thermochemical bond energy terms E(M–X) become available.

Apart from obtaining basic thermochemical data, our primary objectives were to examine in a thermochemical context (i) the concept of p_π–d_π (N–Si) bonding, (ii) group trends, and (iii) the relative 'softness' or class '*b*'[6] behaviour of the cations Me_3M^+. As for (i), we found that E(Si–N) was rather insensitive (76.6 ± 2.5 kcal mol^{-1}) to environment in the five compounds (see above) studied, and hence concluded that π-bonding for SiN was not thermochemically important.[2] Problems (ii) and (iii) are discussed in this paper.

EXPERIMENTAL

Preparation of Organometallic Compounds.—These, with three exceptions, were made by standard procedures and details are in Table 1. Compounds were shown to be pure, after rigorous fractional distillation, by g.l.c. Details for the three exceptions follow.

Chlorotrimethylgermane was made by the method briefly described by Mironov and Kravchenko.[7] A suspension of aluminium trichloride (0·3 g) in 2-chloropropane (12·0 g) was added dropwise to tetramethylgermane[8] (20·0 g) at 0 °C, whereafter the mixture was gradually (1½ h) warmed to 90 °C. Distillation afforded chlorotrimethylgermane (19·0 g, 82%).

Attempts to prepare ethoxytrimethylgermane by a similar method to that used for the silicon analogue (see Table 1) failed, owing to formation of an amine complex. The following route was therefore devised. Bromotrimethylgermane[8] (15·0 g, 1 mol) was added to ethanol-free sodium ethoxide (6·1 g, 1·27 mol) in diethyl ether (50 ml), whereafter the mixture was heated (12 h) under reflux. Distillation afforded *ethoxytrimethylgermane* (6·3 g, 51%) (Found: C, 34·5; H, 8·75. $C_5H_{14}GeO$ requires C, 39·9; H, 8·65%); $\nu_{max.}$ (cap. film): 2987vs, 2925s, 2880s, 1410w, 1380s, 1240s, 1110s, 1070s, 830vsb, 660w, and 612s cm^{-1}; ^{1}H n.m.r. (τ): 9·71 (singlet, Me_3Ge), 8·83 (triplet, Me), and 6·35 (quartet, CH_2).

Chlorotrimethylgermane (10·0 g, 2·2 mol) in diethyl ether (10 ml) was slowly added to di-n-butylthioplumbane (8·8 g, 1 mol) in the same solvent (10 ml), whereafter the mixture was heated (24 h) under reflux. The colour changed from yellow to white. The mixture was filtered and the precipitate was washed with ether (2 × 10 ml). Distillation of the combined filtrate and washings afforded *n-butylthiotrimethylgermane* (4·34 g, 47%) (Found: C, 41·2; H, 8·75. $C_7H_{18}GeS$ requires C, 40·6; H, 8·75%); $\nu_{max.}$ (cap. film): 2978s, 2940s, 2885m, 1462m, 1405w, 1290w, 1255s, 830vsb, 598s, and 560m cm^{-1}; ^{1}H n.m.r. (τ): 9·55 (singlet, Me_3Ge), 9·08 (multiplet, Me), 8·47 (multiplet, β- and γ-CH_2), 7·48 (multiplet, α-CH_2).

The Stoicheiometry of the Hydrolyses.—This was established [equations (1) and (2)] by ^{1}H n.m.r. spectroscopic examination of (*a*) pure starting materials, (*b*) all possible hydrolysis products (pure), and (*c*) actual calorimetric (hydrolysis) products in aqueous 1M-HCl. In each case (*c*), there was no evidence for either unchanged starting materials or unexpected products.

TABLE 1

Preparation of compounds

Compound	Reagents	B.p./(°C/mmHg)	Ref.
$Me_3Si{\cdot}OEt$	Me_3SiCl–EtOH–Et_3N	76/760	*a*
Me_3GeCl	Me_3GeCl–Me_2CHCl–$AlCl_3$	98/750	7
Me_3GeBr	Me_4Ge–Br_2	113·7/760	*b*
$Me_3Ge{\cdot}OEt$	Me_3GeBr–EtONa	101—102/750	See text
$Me_3Ge{\cdot}SBu^n$	Me_3GeCl–$Pb(SBu^n)_2$	66/6	See text
$Me_3Ge{\cdot}NMe_2$	Me_3GeCl–$LiNMe_2$	103/760	*c*
Me_3SnCl	Me_4Sn–$SnCl_4$	154/760	*d*
Me_3SnBr	Me_4Sn–Br_2	164—165/750	*e*
Me_3SnI	Me_4Sn–I_2	64/10	*f*
$Me_3Sn{\cdot}OEt$	$Me_3Sn{\cdot}NMe_2$–EtOH	80/0·1	*g*
$Me_3Sn{\cdot}SBu^n$	Me_3SnOH–Bu^nSH	44/0·05	*h*
$Me_3Sn{\cdot}NMe_2$	Me_3SnCl–$LiNMe_2$	126/760	*i*
$(Me_3Sn)_2NMe$	Me_3SnCl–$MeNH_2$–$LiBu^n$	64/3	*i*
$(Me_3Sn)_3N$	$(Me_3Sn)_2NMe$–NH_3	70/2	*i*

[a] R. O. Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707. [b] L. M. Dennis and W. I. Patnode, *J. Amer. Chem. Soc.*, 1930, **52**, 2779. [c] J. Satgé and M. Baudet, *Compt. rend.*, 1966, **263**, *C*, 435. [d] K. A. Kocheshkov, *Ber.*, 1929, **62**, 996. [e] C. A. Kraus and W. V. Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361. [f] S. N. Naumov and Z. M. Manulkin, *Zhur. obshchei Khim.*, 1935, **5**, 281. [g] J. Lorberth and M. R. Kula, *Chem. Ber.*, 1964, **97**, 3444. [h] E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1965, 1192. [i] K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1965, 1944.

$$(Me_3M)_nX(l) + n\ H_2O\ (\text{in 1M-HCl soln.}) \longrightarrow \left[\frac{n}{2}(Me_3M)_2O + XH_n\right]\text{1M-HCl} \quad (1)$$

$$M = \text{Si or Ge}$$

$$(Me_3M)_nX(\text{l or c}) + nH_2O\ (\text{in 1M-HCl soln.}) \longrightarrow \left[\frac{n}{2}(Me_3Sn{\cdot}OH)_2 + XH_n\right]\text{1M-HCl} \quad (2)$$

$$M = \text{Sn}$$

Calorimetry.—The heats of hydrolysis in 1M-hydrochloric acid were measured with the calorimeter described in ref. 2. The values of ΔH_{obs} in Table 2 are the mean of at least six separate measurements, the uncertainties being twice the standard deviation of the mean.

RESULTS

Enthalpies of Formation.—Equation (3) corresponds to the hydrolysis process and was used to determine the standard enthalpies of formation of the compounds $Me_3Si{\cdot}OEt$ and Me_3GeX (X = Cl, Br, OEt, and SBu^n).

$$Me_3MX(l) + \tfrac{1}{2}H_2O(l) \longrightarrow \tfrac{1}{2}(Me_3M)_2O(l) + HX(55H_2O) \quad (3)$$

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[6] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[7] V. F. Mironov and A. L. Kravchenko, *Izvest. Akad. Nauk S.S.S.R. Ser. khim.*, 1965, **6**, 1026.

[8] D. F. van de Vondel, *J. Organometallic Chem.*, 1965, **3**, 400.

The use of equation (3) was justified because the enthalpies of mixing of $(Me_3Si)_2O$(l) and $(Me_3Ge)_2O$(l) with 1M-hydrochloric acid were found to be less than 0·1 kcal mol^{-1}, and the enthalpies of mixing the molar HX solutions with the molar HCl solution is negligible. For $Me_3Ge\cdot NMe_2$(l), equation (4) is appropriate.

$$Me_3Ge\cdot NMe_2(l) + \tfrac{1}{2}H_2O(l) + HCl(55H_2O) \longrightarrow \tfrac{1}{2}(Me_3Ge)_2O(l) + Me_2NH\cdot HCl(55H_2O) \tag{4}$$

The standard enthalpy of formation of $Me_3Si\cdot OEt$ was determined from the subsidiary data in Table 3. Unfortunately, none of the germanium compounds studied here had an accurately known enthalpy of formation from which to derive the enthalpies of formation of the remaining compounds [*cf.* $(Me_3Si)_2O$ for $Me_3Si\cdot OEt$ and other compounds in ref. 2]. However, the ethalpy of formation of $(Me_3Ge)_2O$(l) can be estimated reasonably accurately as follows.

TABLE 2

Enthalpies of formation and bond energies (all values in kcal mol^{-1})

Compound	$-\Delta H_{obs}$	ΔH_f° (c or l)	ΔH_{vap} [a]	ΔH_f° (g)	E	Bond
$(Me_3Si)_2O$(l)	—	−194·7 ± 1·3 [c]	8·9 [c]	−185·8	105	Si–O
Me_3SiCl(l) [b]	—	−91·8 ± 0·7 [b]	7·2 [c]	−84·6	96 [e]	Si–Cl
$Me_3Si\cdot OEt$(l)	5·7 ± 0·1	−126·4 ± 0·7	8	−118·4	103	Si–O
$(Me_3Ge)_2O$(l)	—	−136·0 ± 4·0 [d]	9	−127·0	82	Ge–O
Me_3GeCl(l)	1·7 ± 0·1	−71·6 ± 2·1	8	−63·6	81 [e]	Ge–Cl
Me_3GeBr(l)	0·5 ± 0·1	−62·1 ± 2·1	9	−53·1	68	Ge–Br
$Me_3Ge\cdot OEt$(l)	6·9 ± 0·2	−95·8 ± 2·2	8	−87·8	79	Ge–O
$Me_3Ge\cdot SBu^n$(l)	−1·1 ± 0·1	−64·7 ± 2·1	10	−54·7	58	Ge–S
$Me_3Ge\cdot NMe_2$(l)	25·8 ± 0·2	−37·1 ± 2·2	8	−29·1	55	Ge–N
$Me_3Sn\cdot OH$(c)	—	−90·8 ± 1·2	15	−75·8	77	Sn–O
Me_3SnCl(c)	3·3 ± 0·1	−58·4 ± 1·2	12	−46·4	75 [e]	Sn–Cl
Me_3SnBr(c)	2·4 ± 0·2	−48·8 ± 1·3	14 [c]	−34·8	61	Sn–Br
Me_3SnI(l)	4·2 ± 0·1	−31·2 ± 1·1 [c]	11·5 [c]	−19·7	45	Sn–I
$Me_3Sn\cdot OEt$(l)	18·3 ± 0·4	−73·1 ± 1·5	10	−63·1	66	Sn–O
$Me_3Sn\cdot SBu^n$(l)	5·1 ± 0·2	−47·1 ± 1·6	10	−37·1	52	Sn–S
$Me_3Sn\cdot NMe_2$(l)	38·2 ± 0·3	−13·3 ± 1·4	9	−4·3	41	Sn–N
$(Me_3Sn)_2NMe$(l)	43·6 ± 0·3	−31·5 ± 2·5	12	−19·5	48	Sn–N
$(Me_3Sn)_3N$(c)	70·2 ± 0·3	−29·2 ± 3·6	15	−14·2	42	Sn–N

[a] All values, except those specified, calculated from b.p.s by use of a Trouton's constant of 22 cal mol^{-1} K^{-1}. Where the condensed state is crystalline a heat of fusion of 3 kcal mol^{-1} has been assumed. The error limits on ΔH_{vap} are of order 2 to 3 kcal mol^{-1}. [b] Data from ref. 2, included to enable calculation of E values for Si compounds. [c] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970. [d] See text for a discussion of this value. [e] Values calculated from enthalpies of formation of tetrahalides (see Table 4) and assumed appropriate for the metal–chlorine bonds in Me_3M–Cl.

TABLE 3 [a]

Subsidiary ΔH_f° for calculation of ΔH_f° (c or l) (all values in kcal mol^{-1})

Compound	ΔH_f°	Compound	ΔH_f°
H_2O(l)	−68·32	Bu^nSH(l)	−29·72 [b]
EtOH(aq.)	−68·9	$Me_2NH,HCl(55H_2O)$	−68·57
$HCl(55H_2O)$	−39·55	$MeNH_2,HCl(55H_2O)$	−69·65
$HCl(53H_2O)$	−39·54	$NH_4Cl(55H_2O)$	−71·48
$HBr(55H_2O)$	−28·72	$(Me_3Si)_2O$(l)	−194·7 [b]
$HI(55H_2O)$	−12·96	$(Me_3Ge)_2O$(l)	−136·0 [c]
		Me_3SnI(l)	−31·2 [b]

[a] All values, except those specified, taken from ref. 5. [b] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970. [c] An extrapolated value from other experimental data; see text.

The enthalpy of formation of Et_6Ge_2O(l) is −148 kcal mol^{-1}.[4] The increment in ΔH_f° on changing from an ethyl group to a methyl group is *ca.* 2 kcal mol^{-1} for most organometallic compounds,[3] whence the value for $(Me_3Ge)_2O$(l) was assumed to be *ca.* −136 kcal mol^{-1}. By use of data from refs. 4 and 5, the enthalpy change for reaction (5) is −9 kcal mol^{-1} (M = Si, X = Cl), −8 kcal mol^{-1} (M = Si, X = Br), −13 kcal mol^{-1} (M = Sn, X = Cl), and −13 kcal mol^{-1} (M = Sn, X = Br). A value of *ca.* −10 kcal mol^{-1} seemed appropriate for M = Ge and X = Cl or Br and, with use of values for Me_4Ge(l) (−41 kcal mol^{-1}),[3] $GeCl_4$(l) (−127 kcal mol^{-1}),[5] and $GeBr_4$(l) (−83 kcal mol^{-1}),[5] gives values of −72 and −62 kcal mol^{-1} for ΔH_f° of Me_3GeCl(l) and Me_3GeBr(l), respectively. Use of the appropriate enthalpies of hydrolysis for equation (3) gives values of −136·8 and −135·8 kcal mol^{-1} for ΔH_f° [$(Me_3Ge)_2O$(l)]. A value of −136·0 ± 4 kcal mol^{-1} therefore seemed appropriate for $(Me_3Ge)_2O$(l), and with subsidiary data from Table 3 yields the enthalpies of formation of the Ge compounds listed in Table 2. [The enthalpy of solution of Bu^nSH(l) in 1M-HCl was found to be less than 0·1 kcal mol^{-1}].

$$\tfrac{3}{4}Me_4M(l) + \tfrac{1}{4}MX_4(l) \longrightarrow Me_3MX(l) \tag{5}$$

The enthalpy of solution of $Me_3Sn\cdot OH$(c) in 1M-HCl was measured and found to be less than 0·1 kcal mol^{-1}, so the enthalpies of hydrolysis of the Me_3SnX compounds are represented to within 0·1 kcal mol^{-1} by equation (6). For the amido-compounds, equation (7) is appropriate.

$$Me_3SnX(l \text{ or } c) + H_2O(l) \longrightarrow Me_3Sn\cdot OH(c) + HX(55H_2O) \tag{6}$$

$$(Me_3Sn)_nNMe_{3-n}(l \text{ or } c) + nH_2O(l) + HCl(55H_2O) \longrightarrow nMe_3Sn\cdot OH(c) + Me_{3-n}NH_n\cdot HCl(55H_2O) \tag{7}$$

The enthalpy of formation of Me_3SnI(l) quoted in Table 3 was used to calculate ΔH_f° [Me_3SnOH(c)], whence the enthalpies of formation of the Sn compounds in Table 2 are derived. The values for crystalline Me_3SnCl and Me_3SnBr are consistent with the literature values of −50·9 ± 2·5 and −44·3 ± 1·0 kcal mol^{-1} for the corresponding *liquid* phases, since enthalpies of fusion in the range 3—5 kcal mol^{-1} would probably be appropriate for these compounds.

Bond Energies.—The chemical significance of the thermochemical data is best described by the energies of appropriate bonds in the molecules. The derivation of bond energies automatically involves drastic approximations such as assuming that the contribution of the Me_3M group to the enthalpy of formation of Me_3MX is independent of the nature of X. Thus, the absolute values of E listed in Table 2 may not be significant, but the relative values probably have chemical relevance. The bond energies were derived from the gaseous enthalpies of formation by use of equation (8).*

$$\frac{1}{n}\,(Me_3M)_nX(g) + HCl(g) \longrightarrow Me_3MCl(g) + \frac{1}{n}\,H_nX(g)$$

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\,[Me_3MCl(g)] + \frac{1}{n}\,\Delta H_f^\circ\,[H_nX(g)] - \frac{1}{n}\,\Delta H_f^\circ\,[(Me_3M)_nX(g)] - \Delta H_f^\circ\,[HCl(g)] \\ &= E(M\text{–}X) + E(H\text{–}Cl) - E(M\text{–}Cl) - E(H\text{–}X) \qquad (8)\end{aligned}$$

As a basis for calculation, E(M–Cl) was taken to have the value in the corresponding tetrachloride (see Table 4). This was an arbitrary choice and the alternative of calculating E(M–Cl) in Me_3MCl from M–CH_3 bond energies from, for example, the tetramethyl compounds, would lead to significantly different values for all the bond energies. However, the *relative* values would remain unchanged and the discussion in the following section depends on either their relative values or the orders of magnitude of the bond energies.

TABLE 4 [a]

Subsidiary ΔH_f° and bond energies for calculation of E values in Table 2 (all values in kcal mol^{-1})

Compound	ΔH_f° (g)	$\bar{E}$	Atom [b]	ΔH_f° (g)
HCl	−22·062	103·2	H	52·095
HBr	−8·70	87·5	O	59·553
			C	171·291
HI	6·33	71·3	Cl	29·082
H_2O	−57·796	110·8	Br	26·741
EtOH	−56·19		I	25·535
H_2S	−4·93	87·9	S	66·636
Bu^nSH [c]	−20·98		N	112·979
NH_3	−11·02	93·4	Si	108·9
$MeNH_2$	−5·49		Ge	90·0
Me_2NH	−4·41		Sn	72·2
CCl_4 [c]	−25·2	78·2		
$SiCl_4$	−157·03	95·6		
$GeCl_4$	−118·5	81·2		
$SnCl_4$	−112·7	75·3		

[a] All values, except that for Bu^nSH, taken from ref. 5.
[b] ΔH_f: of atoms required for calculation of bond energies, E.
[c] J. D. Cox and G. Pilcher, ' Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

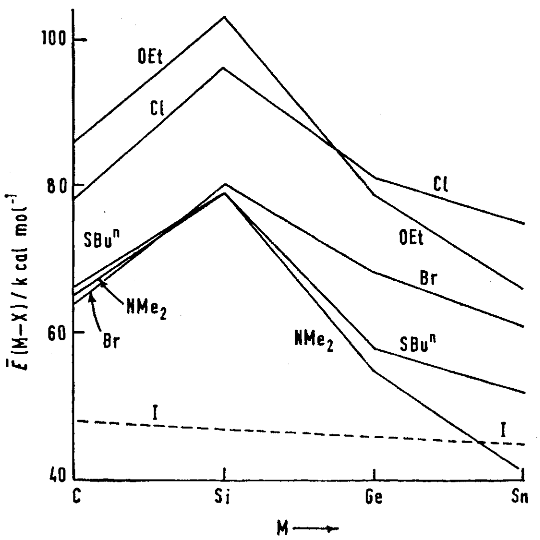
DISCUSSION

Comparison with Published Data.—Our results (Table 2) can in a few cases be compared with earlier data (for comments on Me_3SnCl and Me_3SnBr, see p. 1945).

The value of E(Si–O) of 103—105 kcal mol^{-1} agrees reasonably with other estimates,[9] and that of E(Ge–Br) of 68 kcal mol^{-1} is close to the mean value based on $GeBr_4$, $\bar{E}$(Ge–Br) = 66 kcal mol^{-1}.[9]

The values for E(Sn–Br) and E(Sn–I) of 61 and 45 kcal mol^{-1}, which are relative to $\bar{E}$(Sn–Cl) for $SnCl_4$, differ appreciably from those [10] calculated on the basis of $\bar{E}$(Sn–C) in Me_4Sn. However, the ratios of E(Sn–Br) : E(Sn–I) agree well.

Group Trends.—The Group IV trends for mean bond dissociation energies $\bar{D}$(M–R) in MR_4 and $\bar{D}$(M–H) reveal (data of refs. 9 and 11) a monotonic decrease with increasing atomic number of M (*i.e.*, C > Si > Ge > Sn > Pb). Likewise, a similar trend is observed for E(M–Me) and E(M–H) for the compounds Me_3MX (X = Me [3] or H [12]). In contrast, for the tetrahalides (data of refs. 5, 9, and 13), there is an enhancement for $\bar{E}$(Si–X) (*i.e.*, C < Si > Ge > Sn > Pb). Similar trends are observed for $\bar{E}$(M–X) values taken from Table 2, as shown in the Figure. It is tempting to attribute the enhancement of $\bar{E}$(Si–X) when X is in principle lone-pair possessing to p_π–d_π (Si–X) bonding, and to such π-bonding being more effective for Si than for Ge, Sn, or Pb analogues.



Trends in mean bond energy terms $\bar{E}$(M–X)

The Relative Softness of the Me_3M^+ *Ions.*—The carbonium ion has been described as a ' borderline ' acid.[14] This concept can now be considered in terms of ΔH in a quantitative sense in relation to the other Me_3M^+ ions. Three ideal systems could be taken. These are the F–Cl, OR–SR, and NR_2–PR_2 exchanges, as exemplified by equation (9); from Table 2 and ref. 5,

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* Values for carbon bonds were calculated from appropriate enthalpies of formation from ref. 4, some of the compounds being slightly different from those given in equation (8) (see legend to Figure 1).

[9] T. L. Cottrell, ' The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

[10] J. B. Pedley, H. A. Skinner, and C. L. Chernick, *Trans. Faraday Soc.*, 1957, **53**, 1612.

[11] H. A. Skinner, *Adv. Organometallic Chem.*, 1964, **2**, 49; A. E. Pope and H. A. Skinner, *Trans. Faraday Soc.*, 1964, **60**, 1404; J. V. Davis, A. E. Pope, and H. A. Skinner, *ibid.*, 1963, **59**, 2233.

[12] S. R. Gunn and L. Green, *J. Phys. Chem.*, 1964, **68**, 946.

[13] D. F. Evans and R. E. Richards, *J. Chem. Soc.*, 1952, 1292.

[14] R. B. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; *Chem. in Britain*, 1967, **3**, 103.

enthalpies $\Delta H_{\mathrm{ideal}}$ for reaction (9) are $+2{\cdot}0$ (Si), $-2{\cdot}2$ (Ge), and $-9{\cdot}4$ (Sn) kcal mol^{-1}.

$$\mathrm{Me_3M{\cdot}OR(g) + RSH(g) \longrightarrow Me_3M{\cdot}SR(g) + ROH(g)} \qquad (9)$$

From these data, it is clear that the degree of 'softness' for the species $\mathrm{Me_3M^+}$, based on ΔH, increases with increasing atomic number of M, and we predict that this is the probable trend for other Groups of the Periodic Table. The terms 'hard' and 'soft' are seen as providing an essentially phenomenological description rather than a rationalisation. Features such as polarising power or π-bonding may contribute significantly, but their relative value is unknown, and to some degree is irrelevant to the above conclusion.

Some Chemical and Thermochemical Correlations.—From the ΔH_f° data of Table 2 and elsewhere,[5] it is possible to comment on the significance of thermochemical information in relation to chemical differences among the Group IV elements.

It is established that reactions of equation (9), but for compounds in their standard states, proceed from left-to-right for M = Sn or Pb, but conversely for M = Si or Ge.[15] This is consistent with trends in ΔH/kcal mol^{-1} for reaction (10): $-1{\cdot}3$ (Si), $-5{\cdot}6$ (Ge),

$$\mathrm{Me_3M{\cdot}OEt(l) + Bu^nSH(l) \longrightarrow Me_3M{\cdot}SBu^n(l) + EtOH(l)} \qquad (10)$$

and $-10{\cdot}7$ (Sn). Similar trends show that it is not unreasonable that alkylthio-derivatives may be formed from aqueous solutions for Sn [*e.g.* $\mathrm{(Me_3SnOH)_2}$ or $\mathrm{Me_3SnOR + RSH}$ in $\mathrm{H_2O}$] but not Si or Ge.

Another difference between the Group IV elements is that chlorides $\mathrm{Me_3MCl}$ can be converted into $\mathrm{Me_3MBr}$ by heating under reflux with $\mathrm{BBr_3}$, for M = Sn but not M = Si.[16] Consistent with this, the Sn reaction is more exothermic: ΔH for the condensed-phase reaction = $-1{\cdot}0$ (Si) and $-5{\cdot}3$ (Sn) kcal mol^{-1}.

Finally, aminostannanes cannot generally be obtained from corresponding halides and amines. Reactions between such compounds leads to 1,1-adduct formation [*e.g.*, reaction (11a)], whereas for Si or Ge analogues equation (11b) is appropriate, although initial formation of an adduct is probable.[17]

$$\mathrm{Me_3MCl(l\ or\ c)} + \mathrm{Me_2NH(l)} \left\langle \begin{array}{l} \xrightarrow{\text{(a)}} \mathrm{Me_3MCl{\cdot}Me_2NH(c) + Me_2NH(l)} \\ \xrightarrow{\text{(b)}} \mathrm{Me_3M{\cdot}NMe_2(l) + Me_2NH_2Cl(c)} \end{array} \right. \qquad (11)$$

Trends in ΔH/kcal mol^{-1} for reaction (11b) are: $-22{\cdot}3$ (Si), $-13{\cdot}0$ (Ge), and $-2{\cdot}4$ (Sn). It is clear that equation (11b) is thermochemically much more favourable for M = Si than for M = Sn; the enthalpy of adduct formation [equation (11a)] is likely to be *ca.* -10 kcal mol^{-1}.

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[15] *Cf.* E. W. Abel and D. A. Armitage, *Adv. Organometallic Chem.*, 1967, **5**, 1; H. Schumann, I. Schumann-Ruidisch, and M. Schmidt, in 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1971, vol. 2, p. 297.

[16] P. M. Druce and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 3595.

[17] K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1965, 1944.