BONDING STUDIES OF COMPOUNDS OF BORON AND THE GROUP IV ELEMENTS

VI. MASS SPECTROMETRIC STUDIES ON COMPOUNDS Me_4M AND $Me_3M-M'Me_3$ (M AND M'=C, Si, Ge, Sn, AND Pb): THERMOCHEMICAL DATA

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SUMMARY

The mass spectra of the series of compounds $Me_3M-M'Me_3$ and Me_4M are reported and analysed, where M and M' are C, Si, Ge, Sn, and Pb. Ionisation potentials of the parent molecular ions and appearance potentials of Me_3M^+ and $Me_3M'^+$ fragment ions have been measured. Using known or estimated values for the gas phase standard enthalpies $[\Delta H_f^o (g)]$ of formation of $Me^\cdot$, $Me_3C^\cdot$, Me_3C^+, Me_4M, Me_6C_2, Me_6Si_2, and Me_6Sn_2 yields an overdetermined set of 31 simultaneous equations for the $\Delta H_f^o (g)$ of 27 molecules, radicals, and ions. A least squares analysis thus affords the $\Delta H_f^o (g)$ data for all the species $Me_3M-M'Me_3$, Me_4M, $Me_3M^\cdot$, and Me_3M^+. From these data, values are derived for bond (D) and mean bond $(\bar{D})$ dissociation energies: $D(Me_3M-Me)$, $D(Me_3M-M'Me_3)$, and $\bar{D}(Me_4M)$, as well as mean thermochemical bond energy terms $(\bar{E})$ for Me–M and M–M' bonds in each of these species. Data (in kcal/mole) include

   (*i*). $\bar{E}$(Me–M) in Me_4M (value for M in parentheses): 82.1(C), 68.5(Si), 59.9(Ge), 48.1(Sn), and 32.9(Pb);

   (*ii*). E(M–M') in Me_6M_2: 78.9(C), 68.0(Si), 59.3(Ge), 38.3(Sn), and 33.3(Pb);

   (*iii*). E(M–C) in Me_3M-CMe_3: 66.6(Ge), 53.0(Sn), and 41.6(Pb);

   (*iv*). E(M–Si) in $Me_3M-SiMe_3$: 63.3(Ge) and 56.1(Sn), and

   (*v*). E(Ge–Sn) in $Me_3Ge-SnMe_3$: 53.7.

   Trends are discussed.

INTRODUCTION

   Published values for the ionisation potentials of $Me_3M^\cdot$ radicals are listed in Table 1. The considerable disagreements are doubtless in part due to the variety of techniques employed by different workers. In this study, an attempt has been made to obtain self-consistent values by using a single technique for all our experimental measurements, and to obtain sufficient data to provide an internal check on the results. One of the aims of this work was to provide reliable thermochemical data on organometallic compounds of the Group IV elements, which have been notably lacking[10].

TABLE 1

IONISATION POTENTIALS OF THE Me_3M RADICALS

Radical	IP (eV)	Method[a]	Ref.
$Me_3C^{\cdot}$	7.42 ± 0.07	A	1
	7.45 ± 0.1	B	2
	6.9 ± 0.1	C	3
$Me_3Si^{\cdot}$	7.10 ± 0.15	C	4
	6.94 ± 0.43	C	5
	7.8	D	6
	7.97 ± 0.10	C	9
$Me_3Ge^{\cdot}$	8.0	D	6
$Me_3Sn^{\cdot}$	6.54 ± 0.15	C	7
	6.80 ± 0.3	C	8
	7.10 ± 0.05	B	2
	7.6	D	6
$Me_3Pb^{\cdot}$	7.6	D	6

[a] A: Pyrolysis to produce Me_3C radicals in the mass spectrometer; B: Me_3M radicals produced and ionised in a double-beam mass spectrometer; C: combination of thermochemical and mass spectrometric data; D: not stated (these values were quoted without references or probable errors).

EXPERIMENTAL

The hexamethyl compounds were, in the main, prepared by the general reaction of eqn. (1), while in one case the procedure of eqn. (2) was used.

$$Me_3MLi + Me_3M'X \xrightarrow{\text{THF}} Me_3M-M'Me_3 + LiX \qquad (1)$$
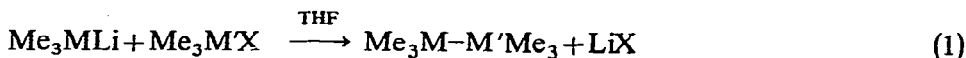
The compounds Me_6Si_2, Me_6Ge_2, and Me_6Sn_2 were gifts from other workers in this laboratory, and Me_6C_2 was obtained from the Aldrich Chemical Co.

$$Me_3SiCl + Me_3GeBr \xrightarrow[\text{cyclohexane}]{\text{K}} Me_3Si-GeMe_3 + Me_6Si_2 + Me_6Ge_2 \qquad (2)$$
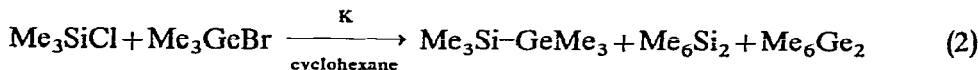
The tetramethyl compounds were prepared by standard literature methods[11], except for neopentane, which was a gift from Dr. J. E. Drake.

All the compounds, except Me_4C, Me_6C_2, and $Me_3Si-GeMe_3$, were purified by distillation under reduced pressure. The hydrocarbons were used without further purification.

The silicon–germanium compound was purified by preparative scale GLC. Purity was verified by elemental analyses (C and H), b.p. (or m.p.), and comparison of IR spectra with those of authentic specimens.

Samples of the hexamethyl compounds were introduced into the A.E.I. MS9 mass spectrometer by evaporation through an all-glass "direct-inlet" probe[12]. Convenient ion currents were obtained by immersing the samples in slush baths. The tetramethyl compounds were introduced via the gas (cold) inlet. The spectra of all the compounds studied were recorded using a 50 eV electron beam, 8 kV accelerating voltage, and a source temperature of 80–100°. The relative abundances of "mono-isotopic" species were calculated by standard procedures[13,22]. The isotopic abun-

dance values used for the combinations Si–Ge, Ge–Sn[14], Ge–Ge[15], and Sn–Sn[16] were those reported in the literature. The abundances of the lead isotopes in the lead-containing compounds were calculated from the mass spectrum of Me_4Pb. These values and the values used for Si–Si and Si–Sn combinations are shown in Table 2.

TABLE 2

ISOTOPIC ABUNDANCES IN Pb, Si_2, AND SiSn CONTAINING COMPOUNDS

Normal m/e	Abundance (%)	No. of combinations contributing of peak
Pb *Compounds*		
204	1.34 ± 0.06	
206	16.12 ± 0.08	
207	21.03 ± 0.08	
208	51.51 ± 0.09	
Si_2 *Compounds*		
56	85.2	1
57	8.6	2
58	5.8	3
59	0.3	2
60	0.1	1
SiSn *Compounds*		
140	0.8	1
141		1
142	0.6	2
143	0.3	2
144	13.0	3
145	7.7	3
146	22.5	3
147	9.1	3
148	32.6	3
149	1.8	2
150	5.3	2
151	0.2	1
152	5.6	2
153	0.3	1
154	0.2	1

The ion abundances of the tetramethyl compounds agree reasonably well with the results of Dibeler[17], and therefore are not listed here. The ion abundances for the hexamethyl compounds are shown in Table 3. Major metal-containing ions of $>1\%$ of the total ion abundance are listed; the abundance of the $C_4H_9^+$ ion from the t-butyl compounds, and the other major hydrocarbon ions from Me_6C_2, are also given.

For ionisation and appearance potential measurements, the mass spectrometer was operated as described previously[18], except that the electron-trap voltage was left unaltered. The heliopot controlling the electron-beam energy was coupled to the photographic recorder so that the appearance of an ion was recorded automatically[19]. The appearance and ionisation potential measurements were interpreted by the

TABLE 3

ION ABUNDANCES FOR IONS FROM HEXAMETHYL COMPOUNDS

Ion (unipositive)	M–M'										
	C–C	C–Ge	C–Sn	C–Pb	Si–Si	Si–Ge	Si–Sn	Ge–Ge	Ge–Sn	Sn–Sn	Pb–Pb
$C_6H_{18}MM'$		4	3	1	12	8	5	7	3	5	2
$C_5H_{15}MM'$	3	6	5	3	20	19	19	18	15	16	12
$C_4H_{12}MM'$				1		1	2	1	2	2	2
C_3H_9MM'	1					1	1	2	2	1	2
C_2H_6MM'								1	1	1	1
C_2H_5MM'								1	1	1	1
CH_3MM'	2								1	1	3
CH_2MM'										1	1
MM'										2	6
$C_3H_{10}M$	2										
C_3H_9M	44	10	23	32	42	35	33	57	33	46	38
C_3H_8M	12										
C_3H_7M	2										
C_2H_7M	6				3	1	1	2	3	1	
C_2H_6M	1				5	1		2	1	4	3
C_2H_5M	13										
CH_5M	7				9	3	5	1	1	1	
CH_4M	2				2						
CH_3M	3				6	1	2	7	6	15	23
H_3M	2										
HM						1		1	1	1	
M										2	6
C_3H_9M'		65	48	35		8	5		7		
C_2H_7M'		1	1	1	1						
C_2H_6M'		2	3	4	8	7			8		
CH_5M'		1			1						
CH_3M'		6	11	16	12	18			15		
CH_2M'		2	1	1							
HM'		2	2	1							
M'		1	3	6			1				

Lossing semi-logarithmic plot method[20]. The results for $Me_3C–SnMe_3$ were also calculated by the extrapolated voltage difference method[21]. Agreement between the two methods was well within experimental error. The ionisation and appearance potentials, and the slush bath temperature used are given in Table 4. Each quoted error represents twice the standard deviation of the mean of the number of measurements also quoted.

DISCUSSION

Mass spectra

In all spectra the ion $C_3H_9M^+$ was the most abundant species. The stability of these ions is associated with their having an even number of electrons and being isoelectronic with the neutral stable Group III molecules; this has been discussed by several authors[22,23]. It is assumed that these ions have structures comparable to the

TABLE 4[a]

IONISATION AND APPEARANCE POTENTIALS OF $Me_3M-M'Me_3$ AND Me_3M-Me COMPOUNDS

Compound	Slush bath (°C)		No. of readings	IP (eV)	AP (eV)	
					Me_3M^+	$^+M'Me_3$
$Me_3C-GeMe_3$		−78	7	8.98±0.12	10.19±0.27	9.91±0.22
$Me_3C-SnMe_3$		−45	7	8.34±0.11	10.03±0.23	9.32±0.16
$Me_3C-PbMe_3$	−34,	−23	7	7.99±0.13	9.45±0.15	8.67±0.21
$Me_3Si-SiMe_3$		−84	8	8.35±0.12	10.22±0.18	
$Me_3Si-GeMe_3$		−78	7	8.31±0.10	10.19±0.12	9.99±0.14
$Me_3Si-SnMe_3$	−78,	−45	7	8.18±0.14	10.18±0.26	9.80±0.24
$Me_3Ge-GeMe_3$		−64	7	8.18±0.11	9.96±0.16	
$Me_3Ge-SnMe_3$		−45	7	8.20±0.10	10.01±0.18	9.85±0.22
$Me_3Sn-SnMe_3$		−45	9	8.02±0.15	9.51±0.22	
$Me_3Pb-PbMe_3$		−23	7	7.41±0.10	9.02±0.14	
Me_3Si-Me			7	9.85±0.16	10.53±0.20	
Me_3Ge-Me			7	9.29±0.14	10.05±0.14	
Me_3Sn-Me			7	8.76±0.12	9.58±0.19	
Me_3Pb-Me			7	8.26±0.17	8.77±0.16	

[a] Tolerances are shown as ± 2 × standard deviations.

t-butyl carbonium ion, which is known to be particularly stable [3,24]. This assumption cannot be proved, but other possible structures, such as carbonium ions of the type $Me_2M(H)C^+H_2$, are thought to be less likely on the following grounds.

(i). In the case of M = Pb, it is highly unlikely that an ion containing Pb–H bonds would be as abundant as is the $C_3H_9Pb^+$ ion found in the mass spectra of the lead compounds. The relative abundances and appearance potentials from organolead compounds are consistent with the trends in results from the other compounds including those containing Me_3C-groups.

(ii). Appearance potential measurements on the ion $C_3H_9Si^+$ derived from $Me_3Si-CH_2Si(H)Me_2$★ showed an unusually long "tail" in the ionisation efficiency curve indicative of ions of the same m/e originating from at least two different sources.

(iii). It seems probable that the ionisation potential of the radical $Me_2Si(H)CH_2$ lies between that of a methyl radical (9.95 eV)[24] and a t-butyl radical (7.42 eV)[1], while the value for the radical Me_3Si is probably lower (see Table 1). However, supposing that the lower appearance potential of the ion $C_3H_9Si^+$ was due to $Me_2Si(H)C^+H_2$ and Me_3Si^+ appears at some higher energy, (say 0.5 eV higher), then the difference of ~0.5 eV would correspond to the energy required to convert Me_3Si^+ to $Me_2Si(H)^+CH_2$ and/or the difference in any excess energy carried by these ions at their production. This is inconsistent with all the other appearance potential measurements and would produce a value for the silicon–silicon bond dissociation energy in Me_6Si_2 of the order of 0.5 eV higher, i.e. ~80 kcal/mole compared with the kinetically-determined[4] value of 69 ± 3 kcal/mole. If, however, the lower appearance potential is indeed due to Me_3Si^+, the results become chemically acceptable.

(iv). Further argument against carbonium ion formation is the identification

★ A sample of this compound was kindly supplied by Dr. J. Simmie of this laboratory.

of metastable ions corresponding to elimination reactions of the types shown in eqn. (3); there is independent evidence on this point[22,23].

$$C_3H_9M^+ \begin{cases} \longrightarrow C_2H_7M^+ + :CH_2 \\ \longrightarrow CH_5M^+ + C_2H_4 \end{cases} \tag{3}$$
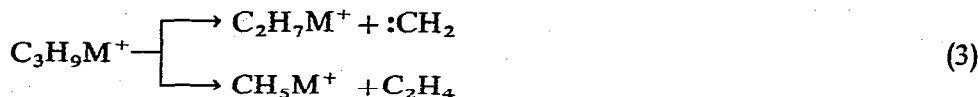
Processes according to equation (3) were established for the compounds Me_4M and Me_6M_2 (M = Si, Ge, Sn) from metastable ion identification. Even in the spectra of methylsilanes $Me_nSiH_{(4-n)}$ $(n=0-4)$[25], hydrogen or hydrocarbons are eliminated [e.g. eqn. (4)], but silicon-containing molecules or radicals are not obtained.

$$(H_3Si-CH_3)^+ \xrightarrow{-H_2} (H_4CSi)^+ \xrightarrow{-CH_4} Si^+ \tag{4}$$
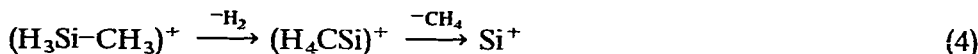
(v). Finally, in the spectra of the compounds Me_4M and Me_6MM' (M and M' = Si, Ge, Sn, Pb), hydrocarbon ions are relatively insignificant, accounting for 4% or less of the total ion current.

The ion abundances from organometallic compounds containing Me_3C groups show similarities to those from the corresponding tetramethyl compounds[17]. For both series of compounds, as the atomic weight of M increases the abundance of the ion Me_3M^+ decreases, whilst those of Me_2M^{+*}, MeM^+, and M^{+*}, as well as of hydrocarbon ions, increase. Although there is excellent agreement between the spectrum obtained for Me_6C_2 and that quoted in the literature[9], there is significant disagreement between the spectrum here obtained for $Me_3C-PbMe_3$ and that reported by Dibeler et al.[26]. There are large discrepancies in the abundance of the parent ion, and of $C_5H_{15}Pb^+$, CH_3Pb^+, Pb^+, and $C_4H_9^+$. Our figures are 1%, 3% 16%, 6%, and 32% respectively, while those obtained by Dibeler et al. are 0.03%, 0%, 29%, 23%, and 1%. Dibeler et al.[26] do not state the inlet temperature and conditions used in their study, but in a previous paper[17] they used 70 eV electrons and source temperatures in the region of 250°. They reported the spectrum of Me_4Pb in both papers and the ion abundances are in very good agreement. Our milder conditions (50 eV electrons, 80° source temperature, and sample held at -23°) may be partly responsible for the differences in spectra.

The assumption may be made that the relative strengths of the metal–metal bonds will be reflected in the relative abundances of the ions containing the intact M–M' bond. The total percentage of such ions is shown in Table 5.

TABLE 5

PERCENTAGE OF IONS CONTAINING M–M' BONDS

C–C	Si–Si	Si–Ge	Si–Sn	Ge–Ge	Ge–Sn	Sn–Sn	Pb–Pb
6	33	29	27	30	25	30	30

Clearly, equating the abundance of M–M' containing ions with bond strengths is incorrect, since, for example, it is generally accepted that the C–C-bond dissociation energy in Me_3C-CMe_3 is much greater than D(Pb–Pb) in $Me_3Pb-PbMe_3$. The ion abundances do, however, reflect the overall rates of formation and decomposition of

ions. For example, the molecule Me_6M_2 just after electron impact is converted into the highly energised ion $Me_6M_2^{+\cdot}$ which has adequate energy to decompose by either of the pathways (5a) or (5b).

$$Me_6M_2^{+\cdot} \begin{array}{c} \xrightarrow{\text{(a)}} Me_5M_2^+ + {}^\cdot Me \\ \xrightarrow{\text{(b)}} Me_3M^+ + {}^\cdot MMe_3 \end{array} \qquad (5)$$

The favoured pathway will depend on the relative rates of cleavage of the M–M′ and M–C bonds in the ions. In the case of Me_6Si_2, it appears that path (b) is more important. In Me_6Pb_2, apparently path (a) is more likely, and several ions are formed as a result of more than one Pb–C bond cleavage. From Table 4, it is seen that there is a general trend that more species containing M–M′ bonds are formed as M–M′ changes from C–C to Pb–Pb. The decomposition of ions such as $Me_5M_2^+$, Me_3M^+, etc., will depend on whether there are further energetically favourable decomposition paths.

The ion abundances shown in Table 3 are in reasonable agreement with those reported for Me_6Ge_2[23,27], Me_6Si_2, Me_6Sn_2, and $Me_3Si–SnMe_3$[27]; except for the following: from Me_6Sn_2, Me_3Sn^+ was found in 46% abundance, compared with 36% reported previously[27]; from $Me_3Si–SnMe_3$, the parent ion, Me_3Si^+, Me_3Sn^+, and $Me_2Sn^{+\cdot}$ were found in abundances 5%, 33%, 5% and 7%, respectively, whereas earlier figures[27] are 2%, 40%, 2% and 5% [the different conditions used (70 eV electrons, source temperature 250°[27]) may, in part, be responsible for the discrepancies].

Ionisation and appearance potentials

In all measurements of appearance potentials, it was assumed that the process of lowest energy producing the ions Me_3M^+ is that of eqn. (6).

$$Me_3M–X \xrightarrow{e^-} Me_3M^+ + X^\cdot \qquad (X = Me, M'Me_3) \qquad (6)$$
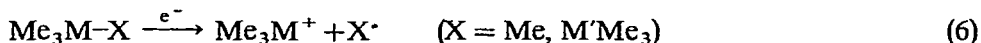
It was also assumed that the ions Me_3M^+ formed in this way have little (< 0.1 eV) or no excess energy. The self-consistency of the results argues in favour of these assumptions. Whilst the ion Me_3M^+ can only arise from $Me_4M^{+\cdot}$ in the spectra of the tetramethyl compounds, it is possible that this ion might arise not only from the ion $Me_6M_2^{+\cdot}$ but also from ions $Me_{6-n}Me_2^+$ for the hexamethyl compounds. Indeed $Me_5M_2^+$ ions are the most abundant M–M′ containing species in all cases. However, the consistency of the results, especially those from compounds such as $Me_3C–PbMe_3$ and Me_6Pb_2, argues against $Me_{6-n}M_2^+$ ions being major sources of Me_3M^+ ions. In the case of $Me_3C–PbMe_3$, the ion $Me_5MM'^+$ most probably has the structure $Me_3C–Pb^+Me_2$ rather than $Me_2C^+–PbMe_3$; the high abundance of the ion $PbMe_3^+$ (35%, base peak) suggests that its source is not various $Me_{6-n}CPb^+$ species, but $Me_6CPb^{+\cdot}$. Furthermore, although metastable species for reaction (7) have been reported[23], metastable peaks corresponding to the formation of Me_3Ge^+ from $Me_5Ge_2^+$ have not been identified.

$$Me_3Ge–GeMe_3^{+\cdot} \rightarrow Me_3Ge^+ + {}^\cdot GeMe_3 \qquad (7)$$

The formation of Me_3C^+ ions from the ion $Me_5C_2^+$ is a real process, as demonstrated by identification of the appropriate metastable species. Presumably, the formation of the ion Me_3C^+ from $Me_6C_2^{+*}$ requires less energy. No evidence was found for metastable species corresponding to the decomposition of $Me_{6-n}M_2^+$ ions into Me_3M^+ ions.

The ionisation and appearance potential results obtained by previous workers are shown in Table 6. There is considerable discrepancy among some of the results,

TABLE 6

Compound	IP (eV)	AP (eV)Me_3M^+	Ref.
Me_3C-CMe_3		9.79 ± 0.1	3
	9.74 ± 0.1		30
$Me_3C-SiMe_3$	9.34 ± 0.06	10.53 ± 0.09	5
		$(Me_3C^+, 11.88)$	
$Me_3C-SnMe_3$		9.50 ± 0.10	8
$Me_3Si-SiMe_3$	8.79 ± 0.08	10.69 ± 0.04	5
		10.0 ± 0.1	35
		10.03 ± 0.1	28
$Me_3Ge-GeMe_3$	8.5 ± 0.1	11.3 ± 0.1	23
$Me_3Sn-SnMe_3$		9.84 ± 0.09	7
	8.08 ± 0.02	9.85 ± 0.16	8
Me_4C		10.29 ± 0.1	3
		10.83 ± 0.1	32
	10.35		31
		10.8 ± 0.1	29
Me_4Si	9.8 ± 0.15	11.3 ± 0.15	33
	9.98 ± 0.03	10.63 ± 0.13	5
	9.81 ± 0.1		34
		10.5 ± 0.1	35
		10.5 ± 0.1	28
	11.2 ± 0.2	12.0 ± 0.2	23
Me_4Ge	9.2 ± 0.2	10.2 ± 0.1	36
	11.2 ± 0.2	11.4 ± 0.2	23
Me_4Sn	8.25 ± 0.15	9.9 ± 0.15	33
		9.72 ± 0.06	7
		9.7 ± 0.2	37
	9.1 ± 0.2	10.8 ± 0.2	23
	8.76 ± 0.02	9.72 ± 0.03	8
Me_4Pb	8.0 ± 0.4	8.9 ± 0.1	33
	9.3 ± 0.2	10.1 ± 0.1	23

probably due to the fact that different conditions and methods of interpretation of ionisation efficiency curves have been used. However, it is interesting to note that the ionisation potential of Me_4Si obtained by photoelectron spectroscopy[34] agrees well with our result.

With regard to the assumption that Me_3M^+ ions are formed with negligible excess kinetic energy, it has been shown that the ion Me_3C^+ derived from Me_6C_2 carries only a very small amount (0.052 eV) of excess energy[38]. It is interesting to note that although H_3C^+ is known to be formed from H_3C-CH_3 with a large amount

$(\sim 1\text{-}2 \text{ eV})^{39}$ of excess energy, the H_3Si^+ and H_3Ge^+ ions from $H_3Si\text{-}GeH_3$ are apparently formed with negligible excess energy[40]. Hess *et al.* have reported the appearance potentials of Me_3M^+ ions from $Me_3C\text{-}SiMe_3$[5]. (We were unable to prepare a pure sample of Me_3CSiMe_3, although several preparative methods were used.) Their value for Me_3C^+ is high, apparently due to excess energy of the order of 1 eV. As with most ionisation efficiency curves of Me_3M^+ ions, the relatively long "tails" to the curves makes their interpretation difficult. With the retarding potential difference method, used by Hess *et al.*[5], it is possible that this is too insensitive. Their values of the appearance potential of Me_3Si^+ from Me_4Si and Me_6Si_2 are also higher (by 0.7 eV in the case of Me_6Si_2) than the values obtained by Davidson *et al.*[35], Haszeldine *et al.*[28], and ourselves (Table 4). From "Stevenson's Rule"[3], it is to be expected that if any ions are formed with excess kinetic energy, then that ion for which the corresponding radical ionisation potential is the greater will carry the excess energy: *i.e.*, from $Me_3C\text{-}MMe_3$, the ion Me_3C^+. The self-consistency of our results points to there being negligible excess energy in the ions formed.

CALCULATION OF STANDARD ENTHALPIES OF FORMATION

The appearance potentials listed in Table 4 and the known or estimated values for the gas phase standard enthalpies of formation of $Me^{\cdot}$, $Me_3C^{\cdot}$, Me_3C^+, Me_4M, Me_6C_2, Me_6Si_2, and Me_6Sn_2 (Table 7) can be represented by the set of Equations (1)

$$\Delta H_j^0 = \sum_i (n_{ij}\Delta H_{f_i}^0) \tag{1}$$

where ΔH_j^0 is the enthalpy change for reactions j (*i.e.*, the appearance potentials for the processes:

$$Me_3MM'Me_3 \rightarrow Me_3M^+ + Me_3M'^{\cdot} + e^-$$

and

$$Me_4M \rightarrow Me_3M^+ + {\cdot}Me + e^- \;;$$

or appropriate enthalpies of formation of the above species); $\Delta H_{f_i}^0$ are the standard enthalpies of formation of the molecules, radicals, and ions involved; and n_{ij} are the number of moles of species i in reaction j (negative for reactants and positive for products). Since equations (1) are overdetermined (31 equations for 27 standard enthalpies of formation) they are more correctly written in the form of equation (2),

$$\delta_j = \Delta H_j^0 - \sum_i (n_{ij}\Delta H_{f_i}^0) \tag{2}$$

where δ_j represents unknown errors associated with the measurements. The best values of $\Delta H_{f_i}^0$ are those which minimize $\Sigma \delta_j \omega_j^2$, where ω_j are weighting factors for the measurements; whence equations (3) are derived.

$$\Delta H_{f_i}^0 \left[\sum_j (n_{ij}n_{kj}\omega_j^2)\right] = \sum_j (n_{kj}\omega_j^2 \Delta H_j^0) \tag{3}$$

The weighting factor ω_j was set equal to one for all equations except those corresponding to the "known" enthalpies of formation $Me^{\cdot}$, Me_4C, and Me_6C_2. In the latter

three cases ω_j was set equal to 10 to ensure that the least squares treatment did not modify significantly these accurately known standard enthalpies of formation.

Equations (3) were solved by standard computing techniques using the ICT 1905 computer at this University, to give the standard enthalpies of formation in Table 8. Residuals were calculated from equations (2), and in every case except Me₄Sn, they were found to be less than the uncertainty intervals quoted in Tables 4 and 7. For Me₄Sn the calculated value is 1.5 kcal/mole different from the input literature value, which has an uncertainty interval of 0.9 kcal/mole. The maximum residual was found to be 1.5 kcal/mole, and the average of the absolute values of the residuals was 0.5 kcal/mole.

The values for $D(\text{Me}_3\text{M}-\text{Me})$, $D(\text{Me}_3\text{M}-\text{M}'\text{Me}_3)$, and $\bar{D}(\text{Me}_4\text{M})$ *(mean bond*

TABLE 7

KNOWN OR ESTIMATED STANDARD ENTHALPIES OF FORMATION (kcal/mole)

Compound	ΔH_f^0
·CH₃	34.80±0.1ᵃ
Me₄C	−40.27±0.25ᵇ
Me₃C·	6.7±1.0ᶜ
Me₃C⁺	178.3±1.0ᶜ
Me₄Si	−47.0±6.0ᵈ
Me₄Ge	−32.0±3.0ᵈ
Me₄Sn	−4.8±0.9ᵇ
Me₄Pb	32.6±0.7ᵇ
Me₆C₂	−53.89±0.5ᵇ
Me₆Si₂	−87.0±2.3ᵉ
Me₆Sn₂	−6.4±2.4ᵇ

ᵃ W. A. Chupka, *J. Chem. Phys.*, 48 (1968) 2337.   ᵇ J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London–New York, 1970.   ᶜ S. W. Benson, *Thermochemical Kinetics*, John Wiley, New York, 1968.   ᵈ From ref. b $\Delta H_f^0\text{Et}_4\text{Ge}(g) = -39.6\pm1.6$ kcal/mole and from unpublished rotating bomb studies (by J. B. P.) $\Delta H_f^0\text{Et}_4\text{Si}(g) = -56.9\pm4.9$ kcal/mole. The increment in ΔH_f^0 on changing from a methyl to an ethyl group is approximately 1.5 to 2.5 kcal/mole for most organometallic compounds (see ref. 10). The difference between the standard enthalpies of formation of Me₄C(g) and Et₄C(g) is 3.75 kcal/mole per alkyl group (ref. b). It was therefore assumed that the standard enthalpies of formation of Me₄Ge(g) and Me₄Si(g) were respectively 8 and 10 kcal/mole higher than the corresponding ethyl compounds.   ᵉ Unpublished rotating bomb studies (by J. B. P.)

dissociation energy) are given in Table 8, these being derived from the appropriate standard enthalpies of formation. There are certain obvious trends in these dissociation energies, but these are best discussed in terms of the energies of the bonds in the various species. These were derived from the "atomic" heats of formation ($\Delta H_{f_a}^0$), *i.e.*, the enthalpy changes for the processes:

$$\text{Me}_4\text{M}(g) \rightarrow \text{M}(g) + 4\,\text{C}(g) + 12\,\text{H}(g)$$
$$\text{Me}_6\text{MM}'(g) \rightarrow \text{M}(g) + \text{M}'(g) + 6\,\text{C}(g) + 18\,\text{H}(g)$$
$$\text{Me}_3\text{M}(g) \rightarrow \text{M}(g) + 3\,\text{C}(g) + 9\,\text{H}(g)$$
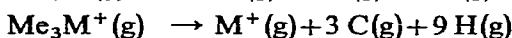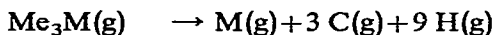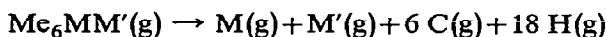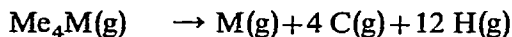$$\text{Me}_3\text{M}^+(g) \rightarrow \text{M}^+(g) + 3\,\text{C}(g) + 9\,\text{H}(g)$$

TABLE 8

DERIVED STANDARD ENTHALPIES (kcal/mole) OF FORMATION AND BOND STRENGTHS

Compound	ΔH_f^0	$-\Delta H_{fa}^{0\,a}$	D	$\bar{D}$	E	Bond
$CH_3{\cdot}$	34.80					
Me_4C	−40.27	1520.0	81.9	87.6	82.1	C–C
$Me_3C{\cdot}$	6.80	1145.7			84.0	·C–C
Me_3C^+	178.20	1234.1			113.5	C^+–C
Me_4Si	−48.25	1465.5	74.4	74.0	68.5	Si–C
$Me_3Si{\cdot}$	−8.63	1098.6			68.3	Si–C
Me_3Si^+	158.56	1119.4			75.2	Si^+–C
Me_4Ge	−32.00	1431.0	69.0	65.4	59.9	Ge–C
$Me_3Ge{\cdot}$	2.25	1069.6			58.6	Ge–C
Me_3Ge^+	164.99	1088.5			64.9	Ge^+–C
Me_4Sn	−3.35	1384.2	65.4	53.6	48.1	Sn–C
$Me_3Sn{\cdot}$	27.22	1026.4			44.2	Sn–C
Me_3Sn^+	184.25	1038.7			48.3	Sn^+–C
Me_4Pb	32.60	1323.0	48.8	38.4	32.9	Pb–C
$Me_3Pb{\cdot}$	46.66	981.7			29.3	Pb–C
Me_3Pb^+	200.07	999.3			35.2	Pb^+–C
Me_6C_2	−53.89	2358.9	67.5		78.9	C–C
Me_6Si_2	−86.38	2266.4	69.1		68.0	Si–Si
Me_6Ge_2	−62.46	2206.1	67.0		59.3	Ge–Ge
Me_6Sn_2	−7.12	2114.3	61.6		38.3	Sn–Sn
Me_6Pb_2	38.71	2018.1	54.6		33.3	Pb–Pb
Me_3CGeMe_3	−55.65	2280.0	64.7		66.6	C–Ge
Me_3CSnMe_3	−24.89	2231.0	58.9		53.0	C–Sn
Me_3CPbMe_3	6.92	2174.0	46.5		41.6	C–Pb
$Me_3SiGeMe_3$	−74.11	2235.9	67.7		63.3	Si–Ge
$Me_3SiSnMe_3$	−49.69	2193.3	68.3		56.1	Si–Sn
$Me_3GeSnMe_3$	−39.65	2165.1	69.1		53.7	Ge–Sn

^{a} The atomic heats of formation were calculated using the following data derived from ref. b of Table 7: $\Delta H_f^0 H(g) = 52.10$, $C(g) = 170.90$, $Si(g) = 108.4$, $Ge(g) = 90.2$, $Sn(g) = 72.0$, $Pb(g) = 46.8$ kcal/mole; and, from C. E. Moore, *Nat. Bur. Stand. Circ.* 467, Vol. 1, 1949, Vol. 2, 1952 and Vol. 3, 1958: $\Delta H_f^0 C^+(g) = 430.67$, $Si^+(g) = 296.33$, $Ge^+(g) = 271.93$, $Sn^+(g) = 241.32$, and $Pb^+(g) = 217.80$ kcal/mole.

The C–H bond energy was assumed to be 99.3 kcal/mole (as in CH_4), whence the values of $E(M-CH)$ and $E(M^+-CH_3)$ were derived. For the species $Me_3MM'Me_3$ it was assumed that the values of $E(M-CH_3)$ were the same as in the corresponding compounds Me_4M and Me_4M'. Thus the quoted bond energy refers only to the central M–M'-bond where M and M' may be C, Si, Ge, Sn or Pb.

Trends in bond energy terms

The reliability of the new thermochemical data summarised in Table 8 may be gauged by the following criteria: (*i*) the small residuals: these attest to the mutual compatibility of the data in the least squares treatment; and (*ii*) they are in satisfactory agreement with literature values for $D(Me_3Si-Me)^4$, $D(Me_3Si-SiMe_3)^{35}$, $D(Me_3Sn-Me)$, $D(Me_3C-SnMe_3)$, and $D(Me_3Sn-SnMe_3)^{40}$. Because of the present state of Group IV organometallic calorimetry, there is some doubt concerning *absolute* values of ΔH_f^0, in particular of Me_4Si and Me_4Ge; however, the values of D are independent of the chosen value of ΔH_f^0 of $Me_4M(g)$.

The trends in E determine trends in D and $\bar{D}$, while D and $\bar{D}$ are determined

by strengths of bonds in both parent molecules and radicals derived therefrom. It is convenient, therefore to comment below upon trends in terms of values of E. The following discussion relates to changes in E in the various species and should be read in conjunction with Table 8.

First considered are C–C bond strengths. The increase in E(C–C) in Me_3C (84.0 kcal/mole) compared with Me_4C (82.1 kcal/mole) is attributed to a hyperconjugative effect. The very large increase in proceeding further to Me_3C^+ (113.4 kcal/mole) is reflected in the difference in first ionisation potential of C (11.26 eV) and Me_3C (7.4 eV). Hyperconjugation is most effective with an *empty* p_π orbital on the central carbon atom giving rise to canonical forms such as:
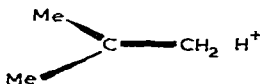
The suggestion that the central C–C bond in Me_3C–CMe_3 is weaker than $E(Me_3C$–Me) by about 3 kcal/mole is attributed to steric strain in the former. However, to some extent this is an artefact, because the total effect is arbitrarily assigned solely to the central C–C bond in hexamethylethane.

When similar trends are examined for the Group IV elements other than carbon, the picture is clearly somewhat altered. The trends in bond strengths in comparing Me_4M with $Me_3M^\cdot$ show an increase in the order Si < Ge < Sn $\simeq$ Pb. It appears that for the radicals Me_3Si and Me_3Ge there is no particular gain in M–C stabilisation compared with Me_4M (in contrast to the $Me_3C^\cdot$ situation) and this is consistent with the fact that these radicals differ from alkyl radicals in being pyramidal (C_{3v}) rather than having D_{3h} symmetry. As yet, comparable information on tin and lead radicals is not available, but perhaps these will prove to resemble those of silicon. In proceeding further to consider $\bar{E}$(M–C) in Me_3M^+, there is clearly significant stabilisation compared with Me_4M or $Me_3M^\cdot$, but the effect is far less pronounced for Si, Ge, Sn, or Pb than for C. This suggests that for the heavier Group IVB elements, the hyperconjugative effect in Me_3M^+ is much less important than when M is C.

A comparison of E(M–C) in Me_3M–CMe_3 and Me_3M–Me leads to the rather curious conclusion that the M–C bonds in the former compounds are stronger than in the tetramethyls. This effect is most pronounced for Pb, with $E(Me_3Pb$–$CMe_3)$ 41.6 kcal/mole compared with $E(Me_3Pb$–Me) 32.9 kcal/mole. One aspect of this effect is not unreasonable: namely, that a bulky t-butyl group will be most comfortably accommodated on the largest available central atom (Pb).

TABLE 9

COMPARISON OF E(M–M') WITH $\frac{1}{2}[E$(M–M) + E(M'–M')]

Compound	E(M–M')	$\frac{1}{2}[E$(M–M) + E(M'–M')]
M–M'		
C–Ge	66.6	69.1
C–Sn	53.0	58.6
C–Pb	41.6	56.1
Si–Ge	63.3	63.7
Si–Sn	56.1	53.2
Ge–Sn	53.7	48.8

Additionally, it is of interest to compare (Table 9) bond energies in heteronuclear pairs $Me_3M-M'Me_3$ with those calculated if the appropriate redistribution reactions from homonuclear partners were thermoneutral. It is clear that only if one member of a heteronuclear pair is carbon such compounds are less stable than their symmetrical products of disproportionation.

Finally, we note that the bond energy terms for carbon to Group IV element bonds $E(C-M')$ decrease in the series,

$$(C-C) > (C-Si) > (C-Ge) > (C-Sn) > (C-Pb)$$

as might be expected on grounds of compatibility of $C-M'$ orbitals. It is interesting to compare this with a similar series for $(N-M')$ bonds in $Me_3M'-NR_2$ compounds[41],

$$(N-C) < (N-Si) > (N-Ge) > (N-Sn)$$
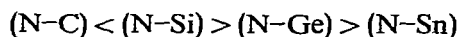
The $(N-M')$ series was rationalised in terms of the importance of π bonding from N to M', which appears to be especially significant at silicon.

ACKNOWLEDGEMENT

REFERENCES

1 F. P. LOSSING AND J. B. DE SOUSA, J. Amer. Chem. Soc., 81 (1959) 281.
2 F. W. LAMPE AND A. NIEHAUS, J. Chem. Phys., 49 (1968) 2949.
3 D. P. STEVENSON, Discuss. Faraday Soc., 10 (1951) 35.
4 I. M. T. DAVIDSON AND I. L. STEPHENSON, J. Chem. Soc. A, (1968) 282.
5 G. G. HESS, F. W. LAMPE, AND L. H. SOMMER, J. Amer. Chem. Soc., 87 (1965) 5327.
6 R. W. KISER, Introduction to Mass Spectrometry and Its Applications, Prentice-Hall, New York, 1965.
7 A. L. YERGEY AND F. W. LAMPE, J. Amer. Chem. Soc., 87 (1965) 4204.
8 A. L. YERGEY AND F. W. LAMPE, J. Organometal. Chem., 15 (1968) 339.
9 J. A. CONNOR, G. FINNEY, G. J. LEIGH, R. N. HASZELDINE, P. J. ROBINSON, R. D. SEDGWICK AND R. F. SIMMONS, Chem. Commun., 6 (1966) 178.
10 H. A. SKINNER, Advan. Organometal. Chem., 2 (1964) 49.
11 G. E. COATES AND K. WADE, Organometallic Compounds, Vol. 1, Methuen, London, 1967.
12 A.E.I., MS9 Instruction Manual, Vol. 1, Section A. 3.6, Fig. 20; A.E.I. Ltd., Manchester, England.
13 J. H. BEYNON, Mass Spectrometry and its Applications to Organic Chemistry, Elsevier, London, 1960.
14 D. B. CHAMBERS AND F. GLOCKLING, J. Chem. Soc. A, (1968) 735.
15 A. CARRICK AND F. GLOCKLING, J. Chem. Soc. A, (1966) 623.
16 D. B. CHAMBERS, F. GLOCKLING, AND M. WESTON, J. Chem. Soc. A, (1967) 1759.
17 V. H. DIBELER, J. Res. Nat. Bur. Stand., 49 (1952) 235.
17a American Petroleum Institute Research Project 44, Thermodynamic Research Center, American Petroleum Institute, Texas, U.S.A. Spectrum No. 56.
18 M. F. LAPPERT, M. R. LITZOW, J. B. PEDLEY, P. N. K. RILEY, AND A. TWEEDALE, J. Chem. Soc. A, (1968) 3105.
19 M. BARBER, Proc. 4th Annual MS9 Mass Spectrometry Users Conference, A.E.I., Manchester, England, 1966, p. 14.
20 F. P. LOSSING, A. W. TICKNER, AND W. A. BRYCE, J. Chem. Phys., 19 (1951) 1254.
21 R. E. WINTERS, J. H. COLLINS, AND W. L. COURCHENE, J. Chem. Phys., 45 (1966) 1931.
22 D. B. CHAMBERS, F. GLOCKLING, AND J. R. C. LIGHT, Quart Rev. Chem. Soc., 22 (1968) 317.
23 J. J. DE RIDDER AND G. DIJKSTRA, Org. Mass Spectrom., 1 (1968) 647.
24 F. W. McLAFFERTY (Ed.), Mass Spectometry of Organic Ions, Academic Press, New York, 1963.

25 G. P. VAN DER KELEN, O. VOLDERS, H. VAN ONCKELEN, AND Z. EECKHAUT, *Z. Anorg. Allg. Chem.*, 338 (1965) 106.

26 E. I. QUINN, V. H. DIBELER, AND F. L. MOHLER, *J. Res. Nat. Bur. Stand.*, 57 (1956) 41.

27 G. VANDENDUNGHEN, *Ph. D. Thesis*, Free University of Brussels, Brussels, Belgium; M. GIELEN personal communication.

28 J. A. CONNOR, R. N. HASZELDINE, G. J. LEIGH, AND R. D. SEDGWICK, *J. Chem. Soc. A*, (1957) 768.

29 J. J. DE RIDDER, AND G. DIJKSTRA, *Recl. Trav. Chim. Pays-Bas*, 86 (1967) 737.

30 J. L. FRANKLIN, *J. Chem. Phys.*, 22 (1954) 1304.

31 K. WATANABE, T. NAKAYAMA, AND J. MOTTL, *J. Quant. Spectrosc. Radiat. Transfer*, 2 (1962) 370.

32 F. W. LAMPE AND F. H. FIELD, *J. Amer. Chem. Soc.*, 81 (1959) 3238.

33 B. G. HOBROCK, AND R. W. KISER, *J. Phys. Chem.*, 65 (1961) 2186.

34 T. N. RADWAN, Thesis, London University, London, 1966.

35 S. J. BAND, I. M. T. DAVIDSON, C. A. LAMBERT, AND T. L. STEPHENSON, *Chem. Commun.*, 14 (1967) 723.

36 B. G. HOBROCK AND R. W. KISER, *J. Phys. Chem.*, 66 (1962) 155.

37 J. L. OCCOLOWITZ, *Tetrahedron Lett.*, 43 (1966) 5291.

38 M. V. GUR'EV, L. V. SUMIN, AND S. A. VOLKOV, *Khim. Vys. Energ.*, 1 (1967) 40.

39 F. H. FIELD, AND J. L. FRANKLIN, *Electron Impact Phenomena*, Academic Press, New York, 1957.

40 W. NEUMANN, *The Organic Chemistry of Tin*, Wiley, London, 1970.

41 J. C. BALDWIN, M. F. LAPPERT, J. B. PEDLEY, AND J. A. TREVERTON, *J. Chem. Soc.*, (1967) 1980; and unpublished observations.

42 W. A. CHUPKA, *J. Chem. Phys.*, 48 (1968) 2337.

43 J. D. COX AND G. PILCHER, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970.

44 C. E. MOORE, *Nat. Bur. Stand. Circ. 467*, Vol. 1, 1940; Vol. 2, 1952; Vol. 3, 1958.

45 S. W. BENSON, *Thermochemical Kinetics*, Wiley, New York, 1968.