ELECTRON IMPACT SPECTROSCOPY OF TETRAMETHYL -SILICON, -GERMANIUM, -TIN, AND -LEAD, TRIMETHYL SILANE AND DIMETHYL MERCURY

by

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INTRODUCTION

An examination of the literature (9, 27) reveals that electron impact data for a large number of molecules has been reported. This type of information is quite obviously lacking for the organometallic compounds. The group IV tetra-alkyls and related organometallics are in most cases low boiling, colorless liquids with significant vapor pressures at room temperatures and could conveniently be studied to provide such data. A comparison of the mass spectra, appearance potentials, and heats of formation for the ions of a group of related compounds such as these can provide useful information on structure and relative probabilities of bond dissociation processes within the group, as well as the fragments formed by electron impact and their energetics being of general interest in radiation chemistry. Therefore, the electron impact spectroscopy of the group IV tetramethyl compounds, trimethylsilane, and dimethyl mercury was studied.

The mass spectral cracking patterns for the group IV tetramethyl compounds, dimethyl mercury and a number of other lead alkyls have been reported previously by Dibeler, et. al. (6, 7, 34). These workers used the spectra obtained in the calculation of the isotopic abundance of carbon, silicon, germanium, tin, and lead and monoisotopic spectra were reported for each compound. Attempts were made to discuss the relation of relative probabilities of ion formation and molecular structure of these compounds.

The ionization and appearance potentials reported here are new; however, an ionization potential of 11.5 ev was reported for tetramethyl lead by Fraser and Jewitt. (12) This is in poor agreement with the value of 8.0 ev reported in this work.

The electron impact spectroscopy of the first member of the series of group IV tetramethyl compounds, neopentane, has been reported recently by Lampe and Field. (28) Appearance potentials and heats of formation for the principal ions of $C(CH_3)_4$ are given. The ionization potential for this compound had been reported previously by D. P. Stevenson (37) as 10.29 ev.

Friedman, Irsa, and Wilkinson (13) have studied the electron impact spectroscopy of a group of ferrocene-type compounds in which they attempted to correlate the data obtained with molecular structure. Mass spectra and appearance potentials for the principal ions in the mass spectra were obtained for the bis(cyclopentadienyl) compounds of vanadium, chromium, iron, cobalt, nickel, rhenium, ruthenium, manganese and magnesium. In each case the dominant specie was the parent molecule-ion. Appearance potentials were reported for $C_{10}H_{10}M^+$, $C_5H_5M^+$, M^+. It is significant to note that the ionization potentials of these compounds approach those of the ionization potentials of the gaseous metal atoms, that only very minor amounts of hydrides were formed, and that the process by which the ions were formed involved the formation of neutral fragments of C_5H_5 and $2C_5H_5$.

A group of these organometallic compounds, tetramethyl lead, tetra-n-propyl lead, diethyl mercury, and di-sec-propyl mercury have been utilized quite recently in which free radicals produced by photoionization were studied with a mass spectrometer. These compounds were pyrolized on a hot platinum filament; spectra were obtained and the appearance of fragments from the radicals in different energy ranges was noted. This work was presented in a paper by Elder, Giese, Inghram, and Steiner at the Ninth Annual Meeting of the ASTM Committee E-14 on Mass Spectrometry. (8)

THEORETICAL CALCULATIONS

A number of different methods have been utilised to calculate ionization potentials. (see, for example, references 26 and 38). G. G. Hall and Sir John Lennard-Jones, in a series of papers beginning in 1949 (19-23, 29-30) recognized that a close relation existed between the vertical ionization potential of a molecule and an energy parameter associated with a molecular orbital (19). A vertical ionization potential is defined as the difference in total electronic energy when one electron is removed at constant internuclear distance. Since ionization removes an electron from a molecular orbital, equations from molecular orbital theory should make it possible to calculate theoretical ionization potentials. However, equations based on electron pair and molecular orbital theories involve a great amount of computation; therefore a new semi-empirical method was proposed in terms of equivalent orbitals. Equivalent orbitals are defined as having the property of being identical with regard to distribution in space and differ only in their orientation. With this new semi-empirical approach, molecules containing the same atoms or groups of atoms could be described by similar equations that link together large numbers of experimental results by means of a small number of empirical parameters and equations.

The secular equation

$$\left| e_{ij} - E\delta_{ij} \right| = 0 \tag{1}$$

proposed by Hall (21) enables us to calculate ionization potentials knowing only the equivalent orbital quantity e_{ij}. This is done semi-empirically using a matrix of equivalent orbital parameters whose diagonal elements are the energies and whose non-diagonal elements represent parameters of interaction between the equivalent orbitals or groups treated as one atom. By comparing the matrices and experimental values for a number of molecules, suitable values for the parameters can be determined and used to predict other ionization potentials. This is easily illustrated by the following application of the theory to the methyl-substituted ethylenes. (22) The ionization potential of propene is the root of the equation.

$$\begin{vmatrix} d - E & x \\ x & m - E \end{vmatrix} = 0 \tag{2}$$

where:

d = double bond parameter (taken as equal to the ionization potential of ethylene).

m = methyl group parameter (taken as equal to the ionization potential of methane).

x = methyl-double bond interaction parameter.

Note that the x interaction on two adjacent C atoms may be neglected.

Using the ionization potential of propene and knowing the d and m parameters, the x parameter is calculated. Then using the x parameter, the ionization potential of 2-butene can be calculated from the roots of the equation:

$$\begin{vmatrix} m - E & x & 0 \\ x & d - E & x \\ 0 & x & m - E \end{vmatrix} = 0 \tag{3}$$

In a similar manner, the y parameter for the interaction between two methyl groups attached to the same atom may then be calculated from 2-methylpropene using the experimentally determined ionization potential of that compound. The ionization potentials for 2-methyl-2-butene and 2,3-dimethyl-2-butene then may be calculated using x and y parameters. Results agreeing quite closely with experimental values can be calculated by this method for the methyl-substituted ethylenes (22), and for a large number of other compounds. (11, 14, 21, 23).

A modified theoretical treatment of the ionization potentials for the studied group IV compounds, based on the Hall equivalent orbital method gives rather good agreement with the observed ionization potentials for these molecules. The modification deals essentially with the parameter for the methyl group--central atom interaction employed in solving the secular equation.

For the molecule $M(CH_3)_4$, where M is carbon, silicon, germanium, tin, and lead, the general determinental equation is:

$$\begin{vmatrix} e - I & 0 & b & 0 & 0 \\ 0 & e - I & b & 0 & 0 \\ b & b & f - I & b & b \\ 0 & 0 & b & e - I & 0 \\ 0 & 0 & b & 0 & e - I \end{vmatrix} = 0 \qquad (4)$$

where:

b = parameter for the interaction of CH_3 with M

f = ionization potential of MH_4

e = ionization potential of CH_4, 13.31 ev

I = ionization potential of $M(CH_3)_4$

Solving the determinant by factoring, one obtains

$$(e - I)^4 (f - I) - 4b^2(e - I)^3 = 0 \qquad (5)$$

Three roots of the equation are given by

$$e = I = 12.31 \text{ ev.} \qquad (6)$$

The other two roots are given by

$$(e - I)\ (f - I) - 4b^2 = 0 \tag{7}$$

which is the general equation for the ionization potentials of these compounds.

In the case of trimethylsilane, the ionization potential, I, is calculated from the expression

$$(e - I)\ (f - I) = 3b^2. \tag{8}$$

For neopentane, $C(CH_3)_4$, $e = f$, and using the b parameter calculated by Franklin (11), the ionization potential is calculated to be 10.2 ev.

The b parameter must now be obtained for the other compounds. The ionization potentials of SiH_4 and GeH_4 are known and have values of 12.2 ev and 12.3 ev respectively. (9) One might not ordinarily expect to find the values of the two ionization potentials so nearly the same, but this is considered reasonable as Si, Ge, and Sn have essentially the same electronegativity. In view of this fact, the f parameter is assigned a value of 12.25 for each of the tetramethyl compounds. The experimentally determined ionization potentials for $Si(CH_3)_4 = 9.8$ ev and for $Sn(CH_3)_4 = 8.25$ ev, (see Results, below) were then used to calculate b parameters for these two compounds. Subsequent interpolation between the calculated b values for $C(CH_3)_4$, $Si(CH_3)_4$, and $Sn(CH_3)_4$ gave b parameters for $Ge(CH_3)_4$ and $Pb(CH_3)_4$. The ionization potentials were then calculated for these two compounds from the general equations given above (equations 7 and 8). Similarly, the ionization potential of trimethylsilane was calculated. The results of these calculations will be discussed in a subsequent section and compared to the experimental determinations.

EXPERIMENTAL

Mass Spectrometry

The mass spectra and appearance potentials reported here were obtained with a Bendix model 12-100 time-of-flight (TOF) mass spectrometer with an analog output system consisting of a monitor and scanner. This instrument has previously been described in detail by a number of workers (4, 14, 15, 24, 25, 43, 44, 45) but will be briefly described here. A schematic diagram of the instrument is given in Figure 1.

The Bendix TOF mass spectrometer gives 10,000 mass spectra per second of any gaseous sample introduced into the source. The ions initially formed are pulsed at 10 kc. into an electric field of about 2800 volts and accelerated to the field free drift tube which has a flight path of about one meter. The instrument operates on the time-of-flight principle. All ions are given the same kinetic energy; therefore their velocities will vary inversely as the square root of mass, the lighter ions having the higher velocities. Since all ions leave the ion source at essentially the same time, those ions of equal mass will tend to bunch and separate from those of a different mass. The ions of a given mass strike the collector cathode and cause secondary electrons to be released which are amplified by the magnetic electron multiplier. A Sanborn model 152 recording system was used to record the ion currents and the pulses are displayed visibly on a Tetronix 545A oscilloscope.

Mass spectra for each of the compounds were obtained at nominal electron energies of 70 ev. The resolution of the instrument is quite good up to mass 150 and is within $\Delta H/H = 0.5$ up to mass 250. ΔH is the height of the overlap between two adjacent peaks of equal height, H. (3) Samples for analysis were contained in glass vacuum bulbs and introduced into the instrument

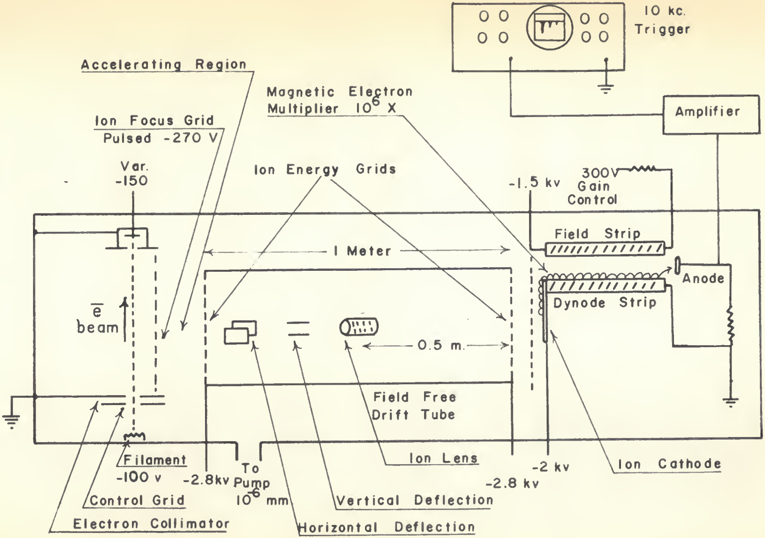

FIGURE I TIME-OF-FLIGHT MASS SPECTROMETER through a glass system which was connected by copper tubing to the stainless steel inlet system. The sample flow was controlled by a stainless steel valve.

Determinations of appearance potentials were made at pressures between 2×10^{-6} and 5×10^{-6} mm Hg obtained with a forepump and a mercury diffusion pump. Liquid nitrogen was used as the coolant in the cold trap-baffle arrangement. The filament was operated at 2.5 amperes and the trap current at 0.125 microamperes. As the electron energy was decreased during a determination, some decrease of the trap current was noted. This trap current decrease apparently has no significant effects on the results obtained, however, since ionization potentials for the rare gases and other molecules determined in the same way were found to compare favorably with literature values. In Table 1, experimental and literature values of ionization potentials for a number of these molecules are summarized. The procedure utilized in determining appearance potentials involved centering one electronic gate of the electron multiplier on the peak on which the determination was being made and another electronic gate on a major isotope of the calibrating gas which also was present. The electron energy was then decreased slowly at recorded intervals. The intensities of the two ions under study were subsequently recorded with the Sanborn system as a function of the electron energy. The ionization efficiency curves such as the ones shown in Figures 2 and 3 were prepared by plotting ion intensities as a function of the electron energy. Appearance potentials were calculated using the method of extrapolated difference described by Warren. (41) Ionization efficiency curves were plotted for each determination and the linear portions of the curves forced parallel. The voltage difference, ΔE, between the two curves at a given current was plotted as a function of the current and the value of ΔE obtained upon

Table 1. Ionization Potential Studies of Some Rare Gas Molecules and CO_2.

Reference Molecule	Molecule Studied	I (e.v.)	Ionization Potentials (e.v.) Calc.	Ionization Potentials (e.v.) Literature (a)
Kr	Ne	7.75 ± 0.3	21.75 ± 0.3	21.56
	Ar	1.60 ± 0.2	15.60 ± 0.2	15.76
	Xe	1.95 ± 0.1	12.05 ± 0.1	12.13
	CO_2	0.40 ± 0.2	13.60 ± 0.2	13.78
Ar	Ne	5.75 ± 0.2	21.61 ± 0.2	21.56
Xe	CO_2	1.90 ± 0.2	14.03 ± 0.2	13.78 (b)

(a) See reference (33)
(b) See reference (39)

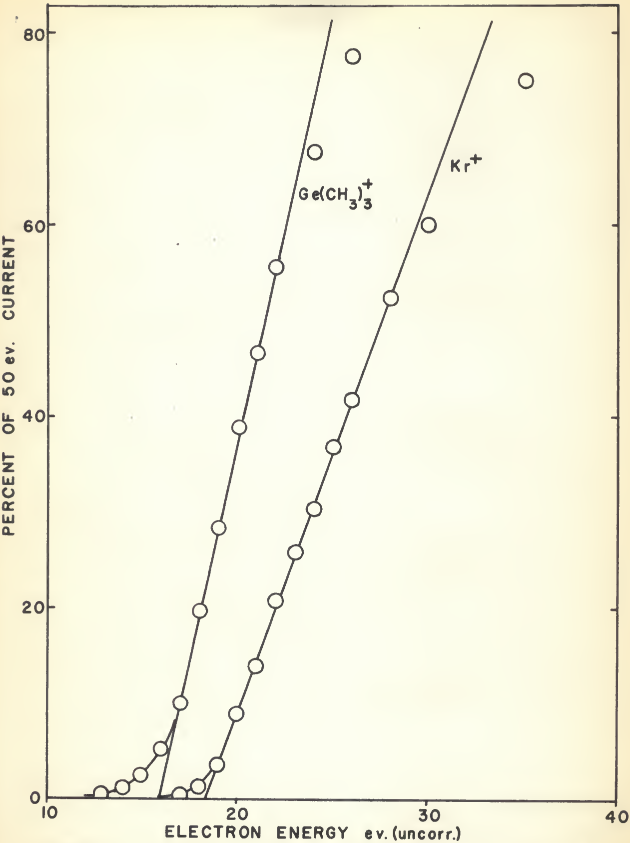

FIGURE 2 TYPICAL IONIZATION EFFICIENCY CURVES

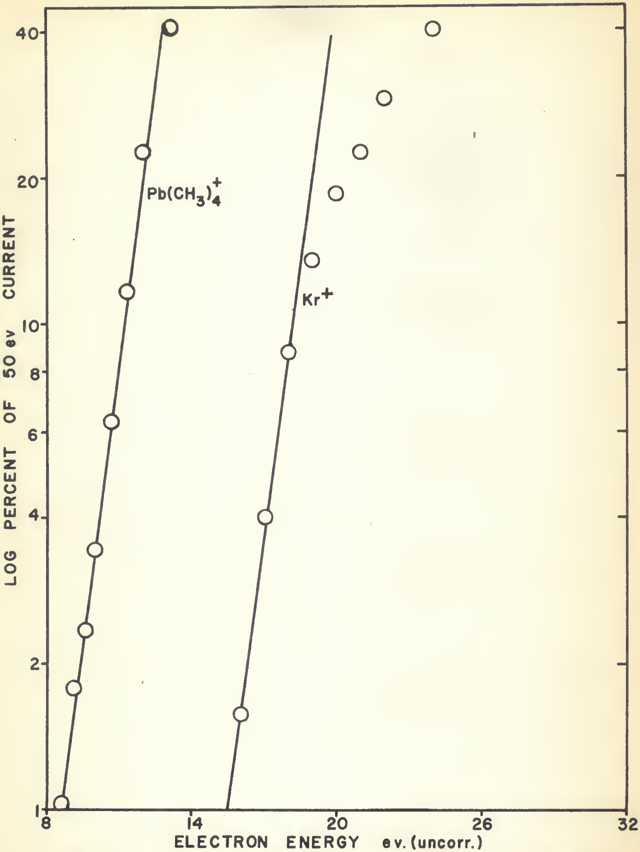

FIGURE 3 TYPICAL IONIZATION EFFICIENCY CURVES

extrapolation to zero current was added algebraically to the ionization potential of the calibrating gas. Krypton or xenon mixed with the compound being investigated was used to calibrate the ionizing voltage. Known spectroscopic values for the ionization potentials of krypton and xenon were used. (33)

Materials Used

Gas chromatographic analyses of most of the compounds were made on a Fisher-Gulf model 160 Partitioner, using a 14 foot column of tri-p-tolyl phosphate on Celite. Separations were satisfactory for our purposes at 80°C; Apiezon-L on Silocel C-22 has also been used for a number of organometallics. (1)

The sample of tetramethyl silicon was obtained from K and K Laboratories. No significant impurities were observed during gas chromatographic analysis of the tetramethyl silicon.

Tetramethyl germanium was obtained from Chemicals Procurement Laboratories. No impurities were noted in the mass spectrum, hence the sample was used as received. Gas chromatographic analysis was not attempted.

In the preparation of tetramethyl tin, freshly distilled $SnCl_4$ was added to an excess of methyl magnesium bromide in diethyl ether and then 10% HCl was added to decompose the excess Grignard and to effect solution of the solids. The ether layer was dried over $MgSO_4$ and distillation gave rather impure tetramethyl tin, as revealed by gas chromatographic and mass spectrometric analysis.

Pure tetramethyl tin was obtained by determining the gas chromatographic peak due to the tetramethyl tin and then trapping it out at 77°K as it was eluted from the column and detector cell of the gas chromatograph. The tetramethyl tin fraction eluted from the gas chromatograph, and trapped, was subsequently found to be quite pure by mass spectrometric analysis.

Tetramethyl lead was prepared from lead chloride and methyl magnesium bromide in diethyl ether. After acidification, the ether layer was dried over $MgSO_4$ and the tetramethyl lead distilled. Gas chromatographic analysis of the sample indicated no impurities.

The sample of trimethylsilane was obtained from Peninsular Chem-Research Inc. The gaseous sample of trimethylsilane was received in compressed form and was transferred directly to sample bulbs on a vacuum line without the sample being exposed to the air. No attempt was made to determine the purity of the sample by gas chromatography, however a small impurity was indicated by the presence of m/e 77 which cannot be identified. This impurity could not have been present in more than 0.5-1.0 percent.

Dimethyl mercury was obtained from K and K Laboratories. Gas chromatographic and mass spectrometric analysis revealed no impurities of any consequence.

RESULTS

The appearance potentials for M^+, MCH_3^+, $M(CH_3)_2^+$, $M(CH_3)_3^+$, and $M(CH_3)_4^+$ in the mass spectra of tetramethyl -silicon, -germanium, -tin, and -lead are summarized in column three of Tables 2, 3, 4, and 5. In Table 6 the appearance potentials are given for the principal ions of trimethylsilane, which include some hydride ions. The appearance potentials are given for MCH_3^+ and $M(CH_3)_2^+$ from dimethyl mercury in Table 7. The probable processes by which the various ions are formed consistent with measured and extrapolated energetics are given in the fourth column. The calculated heats of formation for the ions are given in the last column.

The following heats of formation were used in the calculations with the measured appearance potentials: CMe_4, -37.6 kcal/mole (35, 42); $SiMe_4$, -63 kcal/mole (40); $SnMe_4$, -13.6 kcal/mole (31); $PbMe_4$, 32.6 kcal/mole (16) rather than 3.2 kcal/mole (31); $GeMe_4$, -35 kcal/mole (see below); $SiHMe_3$, -54 kcal/mole (40); $HgMe_2$, -47.5 kcal/mole (32); CH_3, 32.0 kcal/mole (9); CH_2, 68 kcal/mole (9); CH_4, -17.8 kcal/mole (36); C_2H_6, -20.2 kcal/mole (36); C_2H_4, 12.5 kcal/mole (36); H, 52.1 kcal/mole (36); and C_2H_5, 22 kcal/mole (9).

Mass Spectra

The 70 ev mass spectra of these compounds are shown in Figures 4 and 5. The mass spectra of the Group IV tetramethyl compounds and for dimethyl mercury are in essential agreement with the spectra reported by Dibeler, et. al. (6, 7, 34). To the best of the author's knowledge the mass spectrum of trimethylsilane has not been previously reported.

Table 2. Appearance Potentials and Heats of Formation of the Prinicpal Ions of Tetramethyl Silicon.

Ion	% Abundance (Monoisotopic)	Appearance Potential (e.v.)	Process	ΔH_f^+ (kcal/mole)
Si^+	2.5		$Si(CH_3)_4 \rightarrow Si^+ + 4CH_3$(?)	(278) a
$SiCH_3^+$	11.6	17.1 ± 0.4	$\rightarrow SiCH_3^+ + 3CH_3$	235
$Si(CH_3)_2^+$	1.4	13.9 ± 0.3	$\rightarrow Si(CH_3)_2^+ + 2CH_3$	194
$Si(CH_3)_3^+$	82.2	11.3 ± 0.15	$\rightarrow Si(CH_3)_3^+ + CH_3$	166
$Si(CH_3)_4^+$	2.3	9.8 ± 0.15	$\rightarrow Si(CH_3)_4^+$	163

(a) Taken from reference (9).

Table 3. Appearance Potentials and Heats of Formation of the Principal Ions of Tetramethyl Germanium.

Ion	% Abundance (Monoisotopic)	Appearance Potential (e.v.)	Process	ΔH_f^+ (kcal/mole)
CH_3^+		20.1 ± 0.5	$Ge(CH_3)_4 \rightarrow CH_3^+ + Ge + 3CH_3$	254
Ge^+	3.8	19.2 ± 0.5	$\rightarrow Ge^+ + 4CH_3$	279
$GeCH_3^+$	16.7	16.8 ± 0.4	$\rightarrow GeCH_3^+ + 3CH_3$	245
$Ge(CH_3)_2^+$	3.3	14.1 ± 0.2	$\rightarrow Ge(CH_3)_2^+ + 2CH_3$	226
$Ge(CH_3)_3^+$	74.8	10.2 ± 0.1	$\rightarrow Ge(CH_3)_3^+ + CH_3$	168
$Ge(CH_3)_4^+$	1.4	9.2 ± 0.2	$\rightarrow Ge(CH_3)_4^+$	177

Table 4. Appearance Potentials and Heats of Formation of the Principal Ions of Tetramethyl Tin.

Ion	% Abundance (Monoisotopic)	Appearance Potential (e.v.)	Process	ΔH_f^+ (kcal/mole)
Sn^+	5.7	18.1 ± 0.3	$Sn(CH_3)_4 \rightarrow Sn^+ + 4CH_3$	276
$SnCH_3^+$	14.5	15.7 ± 0.4	$\rightarrow SnCH_3^+ + 3CH_3$	253
$Sn(CH_3)_2^+$	8.2	13.1 ± 0.2	$\rightarrow Sn(CH_3)_2^+ + 2CH_3$	225
$Sn(CH_3)_3^+$	69.1	9.9 ± 0.15	$\rightarrow Sn(CH_3)_3^+ + CH_3$	183
$Sn(CH_3)_4^+$	2.0	8.25± 0.15	$\rightarrow Sn(CH_3)_4^+$	177

Table 5. Appearance Potentials and Heats of Formation of the Principal Ions of Tetramethyl Lead.

Ion	% Abundance (Monoisotopic)	Appearance Potential (e.v.)	Process	ΔH_f^+ (kcal/mole)
Pb^+	18.2	15.0 ± 0.5	$Pb(CH_3)_4 \rightarrow Pb^+ + 4CH_3$	251
$PbCH_3^+$	29.3	12.4 ± 0.2	$\rightarrow PbCH_3^+ + 3CH_3$	223
$Pb(CH_3)_2^+$	8.5	11.6 ± 0.2	$\rightarrow Pb(CH_3)_2^+ + 2CH_3$	236
$Pb(CH_3)_3^+$	44.4	8.9 ± 0.1	$\rightarrow Pb(CH_3)_3^+ + CH_3$	206
$Pb(CH_3)_4^+$	0.4	8.0 ± 0.4	$\rightarrow Pb(CH_3)_4^+$	217

Table 6. Appearance Potentials and Heats of Formation of the Principal Ions of Trimethylsilane.

m/e	Relative Abundance	Appearance Potential (e.v.)	Process	ΔH_f^+ (kcal/mole)
15	31.1	14.8 ± 0.5	$SiH(CH_3)_3 \rightarrow CH_3^+ + SiH(CH_3)_2$	(25)[a]
27	7.6	15.3 ± 0.5	$\rightarrow C_2H_3^+ + SiCH_3 + 2H_2$	(73)[a]
			$\rightarrow C_2H_3^+ + SiHCH_3 + H_2 + H$	(21)[a]
28	59.8	13.7 ± 0.3	$\rightarrow Si^+ + CH_4 + C_2H_6$	300
29	17.2	14.2 ± 0.2	$\rightarrow SiH^+ + C_2H_6 + CH_3$	262
			$\rightarrow SiH^+ + C_2H_5 + CH_4$	270
31	10.4	14.3 ± 0.5	$\rightarrow SiH_3^+ + CH_3 + C_2H_4$	231
41	11.4	11.7 ± 0.5	$\rightarrow SiCH^+ + H + C_2H_6 + H_2$	186
42	12.1	10.6 ± 0.3	$\rightarrow SiCH_2^+ + C_2H_6 + H_2$	211
			$\rightarrow SiCH_2^+ + 2CH_4$	226
43	42.8	12.4 ± 0.3	$\rightarrow SiCH_3^+ + CH_4 + CH_3$	218
44	11.0	11.0 ± 0.3	$\rightarrow SiHCH_3^+ + C_2H_6$	220
45	14.7	12.8 ± 0.5	$\rightarrow SiH_2CH_3^+ + C_2H_5$	219
58	27.9	10.3 ± 0.2	$\rightarrow Si(CH_3)_2^+ + CH_4$	201
59	100.0	11.9 ± 0.3	$\rightarrow SiH(CH_3)_2^+ + CH_3$	188
73	53.8	10.9 ± 0.3	$\rightarrow Si(CH_3)_3^+ + H$	146
74	7.1	9.8 ± 0.3	$\rightarrow SiH(CH_3)_3^+$	172

(a) Heat of formation of the silicon-containing radical.

Table 7. Appearance Potentials and Heats of Formation of the Principal Ions of Dimethyl Mercury.

Ion	% Abundance (Monoisotopic)	Appearance Potential (e.v.)	Process	ΔH_f^+ (kcal/mole)
Hg^+	22.4		$Hg(CH_3)_2 \rightarrow Hg^+ + 2CH_3$(?)	(257)[a]
$HgCH_3^+$	54.2	10.4 ± 0.2	$\rightarrow Hg(CH_3)^+ + CH_3$	160
$Hg(CH_3)_2^+$	23.4	8.90± 0.2	$\rightarrow Hg(CH_3)_2^+$	158

(a) See reference (36).

Table 8. Calculated and Observed Ionization of Group IV Tetramethyl Compounds.

Compound	b Parameter	Calc IP (e.v.)	Observed IP (e.v.)
$C(CH_3)_4$	1.55	10.21	10.29[a]
$Si(CH_3)_4$	1.5	(9.8)	9.8[b]
$SiH(CH_3)_3$	1.5	10.1	9.8[b]
$SiH_2(CH_3)_2$	1.5	10.5	
SiH_3CH_3	1.5	11.1	
$Ge(CH_3)_4$	1.85	9.1	9.2[b]
$Sn(CH_3)_4$	2.2	(8.3)	8.25[b]
$Pb(CH_3)_4$	2.5	7.8	8.0[b], 11.5[c]

(a) See reference (37).
(b) This work.
(c) See reference (12).

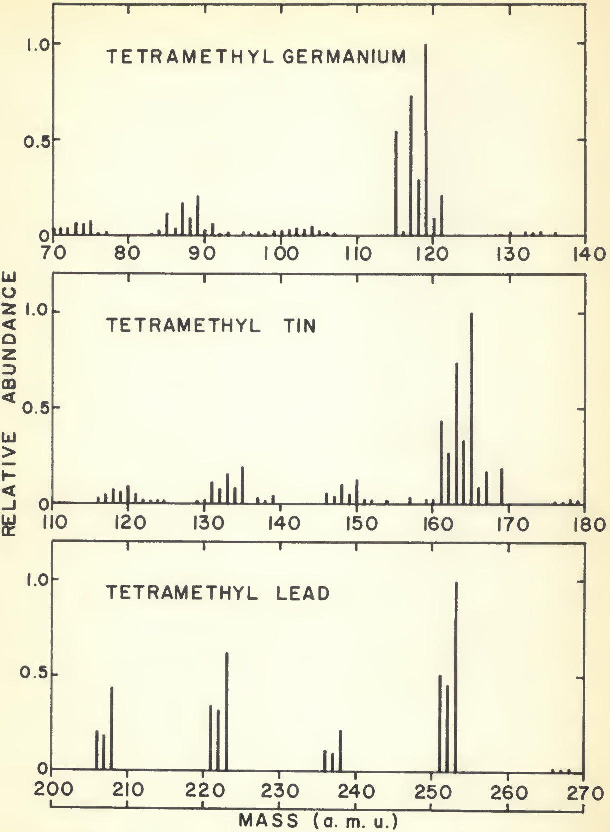

FIGURE 4 MASS SPECTRAL CRACKING PATTERNS

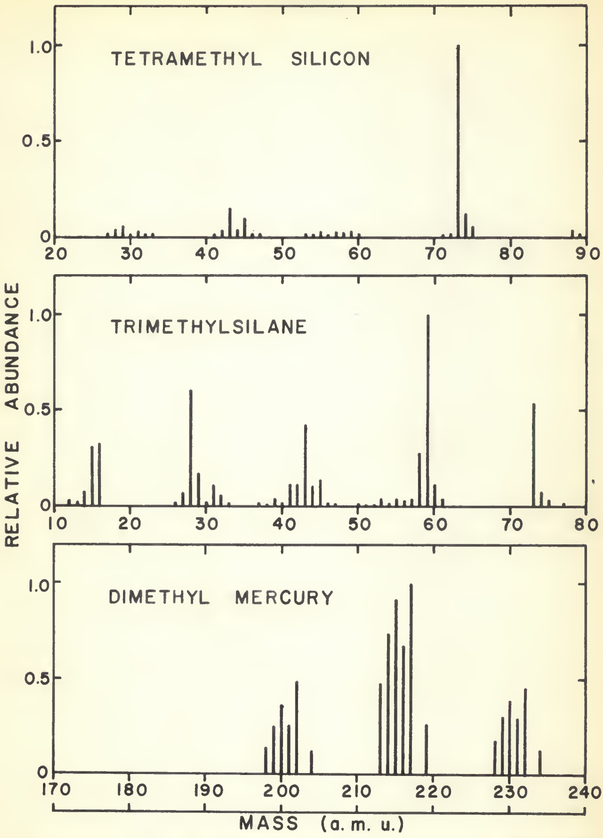

FIGURE 5 MASS SPECTRAL CRACKING PATTERNS

Variation of Ion Abundances with Electron Energy

The manner in which the abundances of the major ions for each of the compounds varies with the voltage is shown in Figures 6 and 7. The curves for tetramethyl -silicon, -germanium, -tin, and -lead and dimethyl mercury involve plotting the percent of the monoisotopic spectrum for each ion against voltage while that for trimethylsilane involves the plotting of percentages of the total polyisotopic spectrum vs voltage, due to the large amounts of hydrides present.

Ionization Potentials

Calculated and observed ionization potentials for the group IV tetramethyl compounds are tabulated in Table 7. Modifying the equivalent orbital treatment due to Hall (see Theoretical Calculations, above) ionization potentials were calculated for tetramethyl lead, tetramethyl germanium, trimethylsilane, and the other methyl substituted silanes. These calculations were based on the parameters shown in Table 7, interpolated and extrapolated from the parameters calculated for neopentane, tetramethyl silicon, and tetramethyl tin using the experimentally determined ionization potentials for these compounds. The value of 7.8 ev calculated for tetramethyl lead is well within our experimental value of 8.0 ± 0.4 (see Discussion). The calculated value of 9.1 ev for tetramethyl germanium is in excellent agreement with an experimental value of 9.2 ± 0.2 ev. The value of 10.1 ev calculated for trimethylsilane is slightly higher than the experimental value of 9.8 ev and indicates an increase in the ionization potentials for the less-substituted silanes, as might be suggested by experimental values for tetramethyl silicon and trimethylsilane and the calculated values for the other silanes.

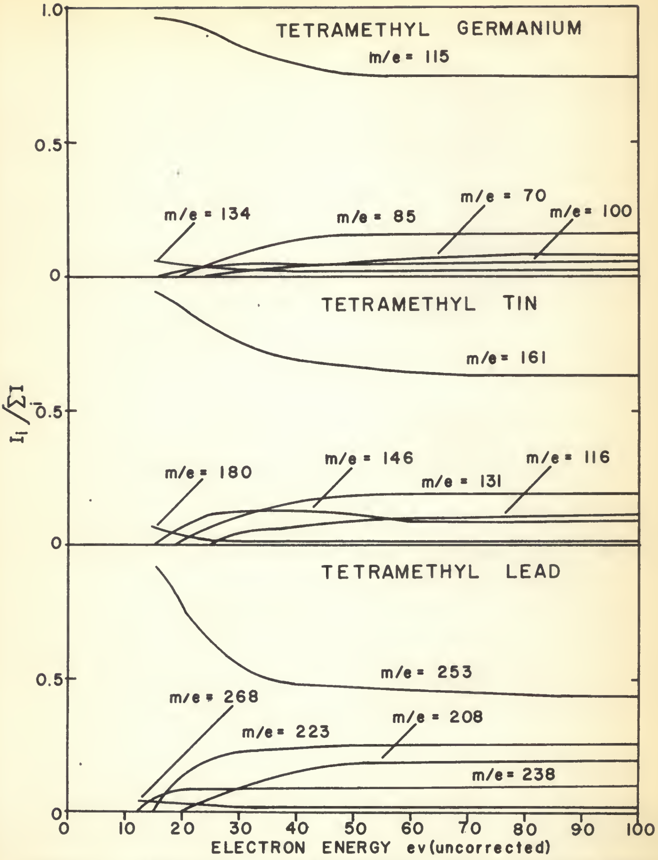

FIGURE 6 VARIATION OF ION ABUNDANCES WITH ELECTRON ENERGY

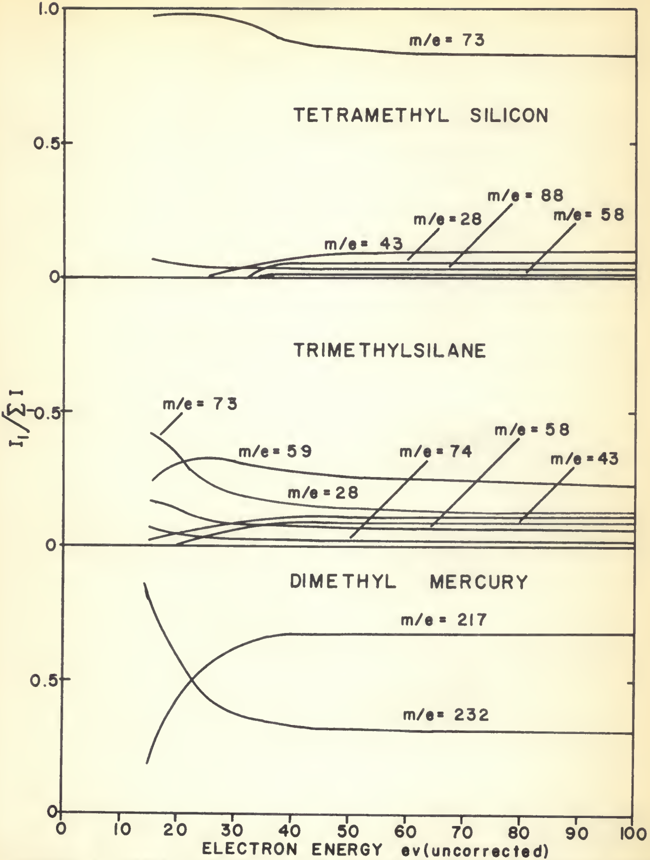

FIGURE 7 VARIATION OF ION ABUNDANCES WITH ELECTRON ENERGY

DISCUSSION

Mass Spectra

The mass spectra of the group IV tetramethyl compounds studied are qualitatively similar, with the abundance of the parent molecule-ion being extremely small and the ion containing three methyl groups being the dominant species. This appears to be a characteristic of many molecules exhibiting this type of symmetry, e. g., CCl_4, CBr_4. It may be noted that the abundances of the smaller fragments, M^+, MCH_3^+, and $M(CH_3)_2^+$, increase significantly with increasing atomic number of the central atom. The decreasing resemblance to the mass spectrum of neopentane (7) is also apparent with increasing atomic number; fewer hydride ions are present in the compounds with heavier central metal atoms.

The mass spectrum of trimethylsilane is similar to that of the tetramethyl compounds in that the dominant specie is formed by the removal of a CH_3 group from the molecule; also, the parent molecule-ion is quite low in abundance. The trimethyl ion is quite abundant as would be expected. Increasing resemblance of the trimethylsilane spectrum to a hydrocarbon spectrum becomes apparent also as large amounts of hydrides are formed, particularly in the m/e 28 to 45 mass range. Rearrangement of CH_3 groups to form ions containing two carbon atoms is also noted with significant amounts of m/e 27 being present which could only be $C_2H_3^+$. It is difficult to determine if any C_2H_6 is present, however, as Si^{30} would interfere.

The mass spectrum of dimethyl mercury shows some similarities to the mass spectra of the group IV compounds with the parent molecule minus a CH_3 group again being the dominant species. The parent molecule-ion is quite abundant however, as well as the metal ion. The formation of hydrides does not seem to be significant. The series of compounds, dimethyl -zinc, -cadmium, and -mercury would be expected to show trends in their mass spectra similar to the trends in the Group IV compounds.

Variation of Ion Abundances with Electron Energy

The variation of ion abundances with electron energy for the group IV tetramethyl compounds are all quite similar with the trimethyl ion being dominant and the tetramethyl ion very small. In each case the trimethyl and tetramethyl ions increase significantly at lower voltages with M^+, MCH_3^+, and $M(CH_3)_2^+$ disappearing at voltages approximating their appearance potential.

In the case of the trimethylsilane, it may be noted that the ions of m/e 73, 58, and 74 are more abundant at lower voltages; the ions of m/e 28, 43, and 59 disappear or decrease markedly at lower voltages. m/e 73 is the ion formed from parent minus a hydrogen, and m/e 58 is formed from parent minus a methyl and a hydrogen. The removal of a hydrogen, and a hydrogen plus a methyl group, is expected to be relatively easy as evidenced by the appearance potentials of m/e 73 and 58 and the Si-H and Si-C bond strengths. The abundance of m/e 74 would be expected to be higher at low voltages and m/e 28, 43, and 59 would be expected to decrease at lower voltages upon noting their appearance potentials.

The curves for dimethyl mercury behave as expected with the dominant $HgCH_3^+$ ion decreasing at lower voltages while the parent molecule-ion increases in abundance. The curves are not quantitative since the Hg^+ ion could not be included due to interference from the background (mercury from the mercury diffusion pump). If the Hg^+ ion could have been included, it would be expected to appear in about 20% abundance at higher voltages, decreasing at lower voltages and disappearing at its appearance potential. The appearance potential of Hg^+ from $Hg(CH_3)_2$ could not be determined because of Hg^+ background interference. The same trends would still be noted in the $HgCH_3^+$ and $Hg(CH_3)_2^+$ ions.

Tetramethyl Silicon

Calculations of the heats of formation for the ions produced from tetramethyl silicon were made using a value of -63 kcal/mole for the heat of formation of tetramethyl silicon (40). Considerable care was taken in the determination of the heats of formation of a number of alkyl silicon compounds by Tannenbaum, Kaye, and Lewenz, (40) and while their values may be slightly low, good agreement is obtained using their reported values of heats of formation of the silicon compounds.

m/e 28. This ion is Si^+. Because of the background at m/e 28, due to N_2^+, it was not possible to determine the appearance potential of the Si^+ ion. All attempts to measure the potential of Si^+ resulted in a value of 15.6 ± 0.1 ev, the accepted value for the ionization potential of N_2^+ (27). However, by comparison with the tetramethyl germanium, tetramethyl tin and tetramethyl lead studies, it is believed that the process for the formation of Si^+ also involves the formation of four CH_3 groups as the neutral fragments. The literature value of $\Delta H_f^+(Si)$ is 278 kcal/mole. (9, 36)

m/e 43. This ion could only be $SiCH_3^+$ on the basis of interpolations between the heats of formation of the other ions, and from an estimation of the energy required to remove successive methyl groups; it is considered reasonable to have three CH_3 groups as the neutral fragments. The value of the appearance potential and the thermochemical calculations rule out $CH_3 + C_2H_6$ as neutral fragments. Thus one calculates that $\Delta H_f^+(SiCH_3) = 235$ kcal/mole.

m/e 58. This ion is $Si(CH_3)_2^+$. Considering the neutral fragments formed to be $2CH_3$, a heat of formation for $Si(CH_3)_2^+ = 194$ kcal/mole is calculated. This value is intermediate between $\Delta H_f^+(Si)$ and $\Delta H_f^+(SiMe_4)$, as would be expected; thus the assignment of two CH_3 groups as the neutral fragments.

m/e 73. This ion is the dominant species in the mass spectrum of tetramethyl silicon and is $SiC_3H_9^+$. It is presumed that the structure is that given by $Si(CH_3)_3^+$. Energetics dictate that the neutral fragment be CH_3. On this basis it is calculated that $\Delta H_f^+(SiMe_3)$ = 166 kcal/mole.

m/e 88. This is the parent molecule-ion. The heat of formation calculated for $Si(CH_3)_4^+$ from the determined appearance potential is 163 kcal/mole.

Tetramethyl Germanium

The heat of formation for this molecule has not to the author's knowledge been reported in the literature. The calculations of the heats of formation for the ions produced from tetramethyl germanium are based upon an estimated value of -35 kcal/mole. This estimation is made on the basis of interpolation between the experimentally determined heats of formation for tetramethyl silicon, -tin, and -lead, and by calculations based on the method due to Franklin. (10) Calculations of heats of formation based upon this value appear to be reasonable. Measurements were made using the germanium isotope of mass 70 in order to minimize the effect of hydride formation. Hydride formation is quite apparent in the mass spectrum but no significant effects were noted in the measurement of appearance potentials of an ion using both the isotopes of mass 70 and 74. The appearance potential of the parent molecule-ion was determined using the isotope of mass 74 exclusively to obtain greater detection sensitivity.

m/e 15. The lack of heats of formation for radicals containing germanium does not prevent the calculation of the heat of formation for this ion which is CH_3^+. From the appearance potential one can see that the neutral fragment is not $Ge(CH_3)_3$. The energetics do favor the accompanying formation of the neutral fragments Ge + $3CH_3$.

m/e 70. This ion can only be Ge^+. The calculation of its heat of formation gave a value of 279 kcal/mole considering the neutral fragments formed to be four CH_3 groups. This is in quite good agreement with the literature value for $\Delta H_f^+(Ge) = 267$ kcal/mole (36). Thus the energetics rule out any process involving the formation of molecules containing two carbon atoms. One might also arrive at the same conclusion on the basis of comparison with the other group IV tetramethyl compounds and interpolation between the heats of formation for the other ion.

m/e 85. The heat of formation for this ion, $GeCH_3^+$, is 245 kcal/mole considering the formation of three CH_3 groups as neutral fragments. If the neutral fragments were $C_2H_6 + CH_3$, $\Delta H_f^+(GeCH_3) = 328$ kcal/mole, a value considered to be unreasonably large.

m/e 100. This ion is $Ge(CH_3)_2^+$. The process is believed to involve the formation of two CH_3 groups as neutral fragments. The heat of formation of the ion is then 226 kcal/mole. Considerations of approximate energies needed to remove subsequent methyl groups and interpolation between the heats of formation of the other ions also lead to the conclusion that two CH_3 groups are the neutral fragments. Hydrides were apparent in the mass spectrum in this region, but it is believed they did not interfere with the determination of the appearance potential of this ion.

m/e 115. The trimethyl ion, $Ge(CH_3)_3^+$, is the dominant species in the mass spectrum of tetramethyl germanium and is believed to be formed simply by the removal of a CH_3 group in the dissociation subsequent to the ionization. The heat of formation for $Ge(CH_3)_3^+$ is calculated to be 168 kcal/mole.

m/e 134. The process for the formation of the parent molecule-ion is ionization. The heat of formation of $Ge(Me)_4^+$ is calculated to be 177 kcal/mole. Good reproducibility (for repetitive determinations) was obtained of the ionization potential of tetramethyl germanium in spite of the low abundance of the ion. The experimentally determined ionization potential, 9.2 ± 0.2 ev, is in good agreement with the value of 9.1 ev calculated using the modified orbital treatment. (see Theoretical Calculations, above).

Tetramethyl Tin

The heat of formation for this molecule was reported by Lippincott and Tobin (31) as -13.6 kcal/mole; this agrees reasonably well with approximate calculations based on Franklin's method (10) and using a heat of formation of -38.1 kcal/mole for tetraethyl tin (17, 32). Calculations of heats of formation for the various ions from $SnMe_4$ are based upon this value. To eliminate any possible interferences due to hydride formation, the measurements of appearance potentials were made using the tin isotope of mass 116, except for the parent ion, where the tin isotope of mass 120 was utilized to achieve greater detection sensitivity, as well as to prevent determining the appearance potential of the ion of the mass of parent-minus-hydrogen.

m/e 116. This ion can be only Sn^+ and the calculation of its heat of formation gave a value of 276 kcal/mole, considering the neutral fragments to be four CH_3 groups. Although this is greater than the value of 243 kcal/mole reported in the literature (36) any other process is incompatible with the energetics.

m/e 131. The heat of formation of this ion, $SnCH_3^+$ is 253 kcal/mole if accompanying it, three CH_3 groups are formed as the neutral fragments. Assuming the neutral fragments to be $C_2H_6 + CH_3$, a value of $\Delta H_f^+(SnCH_3) = 337$ kcal/mole is calculated; this is considered to be too great, and thus discarded as a possible process.

m/e 146. This ion is $Sn(CH_3)_2^+$. The process is considered to be the same as for silicon, germanium, and lead with two CH_3 neutral fragments formed. Considerations of the approximate energy necessary to remove a methyl group and of the fact that the energy for accompanying formation of an ethane molecule would lead to a much lower appearance potential, it is concluded that the neutral fragments are two CH_3 radicals. Thus, $\Delta H_f^+(SnMe_2) = 225$ kcal/mole.

m/e 161. The heat of formation for the dominant species in the tetramethyl tin spectrum, $Sn(CH_3)_3^+$ is 183 kcal/mole for the process involving the foundation of the neutral fragment CH_3. From energetic considerations, this is the only possible process for the formation of this ion.

m/e 180. The heat of formation for the parent molecule-ion, $Sn(CH_3)_4^+$, is 177 kcal/mole; the process of its formation involves the removal of a single electron. Because the tin -121 isotope does not occur naturally, the appearance potential of the ion with $m/e = 180$ definitely is to be attributed to $Sn^{120}(CH_3)_4^+$ and not to $Sn^{121}(CH_3)_3CH_2^+$. The ionization potential of $Sn(CH_3)_4^+$ was found to be 8.25 ± 0.15 ev.

Tetramethyl Lead

These calculations are based on the heat of formation of 32.6 kcal/mole as determined by Good, et. al. (16) This value differs significantly from the value of 3.2 kcal/mole reported by Lippincott and Tobin. (31) Lead has four naturally occurring isotopes; it would have been desirable to have made appearance potential measurements on the isotope of lowest mass to minimize any possible contribution from hydride formation. This was not possible because the isotope with lowest mass only has an abundance of 1.3%; the ions containing isotope of mass 208 were therefore selected to be used in the appearance potential measurements.

m/e 208. This ion is Pb^+, and is the most abundant isotope of lead.

On the basis of the comparison of the literature value of $\Delta H_f^+(Pb)$ = 219 kcal/mole (36) with $\Delta H_f^+(Pb)$ = 251 kcal/mole, calculated for the accompanying formation of four neutral methyl fragments, it is believed that the process of formation of the Pb^+ ion from tetramethyl lead to be that shown in Table 5. The energetics rule out any possible formation of ethane by both the C_2H_6 + $2CH_3$ and the $2C_2H_6$ processes.

m/e 223. This ion is $PbCH_3^+$, again with the possibility of some hydride being present, although near the threshold for formation the contribution of hydrides is not considered to be significant. Consideration of the approximate energy necessary to remove a methyl group, and interpolating between the heats of formation for the other ions, the process is believed to involve the formation of three CH_3 radicals as neutral fragments. Therefore, the heat of formation for this ion is calculated to be 223 kcal/mole.

m/e 238. The heat of formation of this ion, $Pb(CH_3)_2^+$, is calculated to be 236 kcal/mole. Energetics indicate that the process given in Table 5 is the dominant one, involving two methyl groups as neutral products of the dissociative ionization process.

m/e 253. This is the dominant ion in the mass spectrum of tetramethyl lead; it is $Pb(CH_3)_3^+$, formed by the removal of a methyl group subsequent to ionization of the parent molecule. The heat of formation for this ion is calculated to be 206 kcal/mole.

m/e 268. The parent ion, $Pb(CH_3)_4^+$ is of extremely small abundance, and the ionization potential was quite difficult to determine. Only fair agreement was obtained between numerous determination; therefore an error range of ± 0.4 ev was assigned to the value of the ionization potential determined. The agreement of this experimental result with the calculations made on the basis of the modified equivalent orbital treatment substantiates our experimental result (see Table 8). Thus, $\Delta H_f^+(PbMe_4)$ = 217 kcal/mole.

The ionization potential of 8.0 ± 0.4 ev herein reported is 3.5 ev lower than that reported by Fraser and Jewitt (12). The values reported for the ionization potentials of the bis-cyclopentadienyl-metal compounds (13) suggests that the ionization potential for tetramethyl lead is indeed much lower than 11.5 ev, and should be near to that of the gaseous metal atom. Again our result of 8.0 ev agrees with these conclusions. It may be noted that the ionization potentials of the tetramethyl organometallics of group IV decrease in a regular fashion, as expected.

Dimethyl Mercury

The heat of formation for dimethyl mercury has been reported as -47.5 kcal/mole by Long and Norrish (32). The heats of formation for the ions, $Hg(CH_3)_2^+$ and $HgCH_3^+$, are based upon this value. All determinations were made on ions containing the mercury isotope of mass 200; hydride formation is not considered significant.

m/e 200. Interference from the background due to the mercury diffusion pump made it impossible to determine the appearance potential of this ion. All attempts to determine the appearance potential gave the value for the ionization potential of mercury (10.4 ev) (27). The appearance potential of this ion would be expected to be considerable higher than this. The literature value of heat of formation of Hg^+ is 257 kcal/mole (36). Comparison of this case with the group IV tetramethyl compounds would suggest the formation of two CH_3 groups as neutral fragments.

m/e 215. This ion can only be $HgCH_3^+$ and is the dominant ion in the mass spectrum of dimethyl mercury. The only probable process for its formation involves the accompanying formation of a CH_3 group. The heat of formation of formation for the $SiHMe_2$ radical is not available, thus the heat of formation of CH_3^+ cannot be calculated. Using a value of 262 kcal/mole (9) for the heat of formation of this ion, however, the heat of formation of the $SiHMe_2$ radical is calculated to be 25 kcal/mole.

m/e 27. The absence of heats of formation for neutral fragments containing silicon again prevents the calculation of the heat of formation of this ion which is $C_2H_3^+$. A possible process for the formation of this ion involves the formation of $SiCH_3 + 2H_2$ as neutral fragments. Also possible is the formation of $SiHCH_3 + H_2 + H$. Taking the heat of formation of $C_2H_3^+$ as 280 kcal/mole, (9) either the heat of formation for the $SiCH_3$ radical would be 73 kcal/mole or the heat of formation of the $SiHCH_3$ radical would be 21 kcal/mole. The energetics do not allow a differentiation between these two processes.

m/e 28. This ion is Si^+ with undoubtedly some contribution from N_2^+. In the case of trimethylsilane, fortunately, the presence of background N_2^+ does not prevent the determination of the appearance potential of Si^+ as it did with tetramethyl silicon. The appearance potential, 13.7 ± 0.3 ev, falls well below the ionization potential of N_2^+, 15.6 ev, and thus no significant interference is noted. Consideration of various processes involving the formation of different neutral fragments leads one to a process involving the formation of $CH_4 + C_2H_6$. The energetics indicate this to be the process; the calculated heat of formation, 300 kcal/mole, compares fairly well with the literature value of 278 kcal/mole (9). Any other process is incompatible with the energetics.

m/e 29. The availability of a literature value for the heat of formation of this ion, which is SiH^+, makes it possible to determine the process that is taking place. The formation of this ion could involve three CH_3 groups or $CH_3 + C_2H_6$. The latter process is indicated by the energetics, and therefore the heat of formation of SiH^+ is 262 kcal/mole, which compares favorable with the value of 267 kcal/mole for $\Delta H_f^+(SiH)$, as determined in a study of SiH_4 (9). However, the reaction $SiHMe_3 \rightarrow SiH^+ + CH_4 + C_2H_5$ leads to $\Delta H_f^+(SiH) = 270$ kcal/mole. It is not possible on the basis of energetics to distinguish between these two processes. The high-resolution technique of Beynon (2) would be helpful in solving this problem.

<u>m/e 31</u>. The absence of significant amounts of ions of m/e 30 indicated that this ion is SiH_3^+. The literature value for the heat of formation of this ion is 214 kcal/mole (9). It is believed that the process involves the formation of $CH_3 + C_2H_4$; therefore the heat of SiH_3^+ is calculated to be 231 kcal/mole, in reasonable agreement with the literature value. The energetics rule out the processes involving the formation of neutral fragments C_3H_7, and $CH_3 + 2CH_2$.

<u>m/e 41</u>. This ion is $SiCH^+$ and is formed by a process which produces $C_2H_6 + H + H_2$ as the neutral fragments. Therefore the heat of formation of $SiCH^+$ is 186 kcal/mole. This conclusion is drawn as the heat of formation for any other possible process is not reasonable. The low value of the appearance potential, 11.7 ± 0.5 ev, also indicates that the process must involve formation of a neutral product that does not require energy for formation.

<u>m/e 42</u>. This ion could only be $SiCH_2^+$ and has a calculated heat of formation of 210 kcal/mole, if its formation is accompanied by the formation of $C_2H_6 + H_2$ as neutral fragments. The process for the formation of two methane molecules is also possible, giving a heat of formation for $SiCH_2^+ = 226$ kcal/mole. The low appearance potential of 10.6 ± 0.3 ev suggests also that the process involves neutral fragments which do not require energy for formation.

<u>m/e 43</u>. The shapes of the ionization efficiency curves obtained in

determinations of the appearance potential of this ion indicate that two processes are occurring. It was not possible, however, to separate the two or more processes occurring. The appearance potential determined was 12.4 ± 0.3 ev. Since this ion can only be $SiCH_3^+$, and since it was found that $\Delta H_f^+(SiCH_3)$ = 234 kcal/mole from the tetramethyl silicon study, it is believed that the formation of this ion involves the production of neutral fragments of CH_4 + CH_3. $\Delta H_f^+(SiCH_3)$ is then calculated to be 218 kcal/mole, in fair agreement with the value of 234 kcal/mole.

m/e 44. This ion is $SiHCH_3^+$ and the heat of formation calculated, considering the accompanying formation of the neutral fragment C_2H_6, is 220 kcal/mole. This process is selected on the basis of interpolation between the heats of formation of Si^+, SiH^+, $SiH(CH_3)_2^+$ and $SiH(CH_3)^+$ which were established by other evidence in this work. (See Table 2).

m/e 45. The heat of formation of this ion, $SiH_2CH_3^+$, has not previously been reported. The production of the $SiH_2CH_3^+$ ion is believed to be accompanied by the neutral fragment C_2H_5. The heat of formation of $SiH_2CH_3^+$ then is calculated to be 219 kcal/mole.

m/e 58. This ion could only be $Si(CH_3)_2^+$. The low appearance potential of this ion, 10.3 ± 0.2 ev, suggests that methane is formed as the neutral fragment. Therefore, the heat of formation of $Si(CH_3)_2^+$ is 201 kcal/mole, in good agreement with the heat of formation of 193 kcal/mole for $Si(CH_3)_2^+$ determined in the tetramethyl silicon study.

m/e 59. The energetics for the formation of the dominant ion in the mass spectrum of trimethylsilane, $SiH(CH_3)_2^+$, dictate that the neutral fragment formed be CH_3. Therefore, the heat of formation calculated for $SiH(CH_3)_2^+$ is 188 kcal/mole.

m/e 73. This ion has been conclusively established to the author's satisfaction as m/e 73 and is $Si(CH_3)_3^+$, which is quite abundant in the mass spectrum of trimethylsilane. The heat of formation for this ion is therefore 146 kcal/mole, calculated assuming the neutral fragment to be a hydrogen atom. This can be the only process for formation of this ion, but the value of 146 kcal/mole for $\Delta H_f^+(SiMe_3)$ appears low compared to the heat of formation of $Si(CH_3)_3^+$ = 165 kcal/mole calculated from tetramethyl silicon study.

m/e 74. The abundance of the parent molecule-ion for trimethylsilane is quite small in the mass spectrum. Undoubtedly a significant contribution to the m/e 74 peak is made by $Si^{29}(CH_3)_3^+$. Several determinations of the ionization potential, using m/e 74, and in one case m/e 75, gave good agreement. This ion is formed by the removal of a single electron and its heat of formation is calculated to be 172 kcal/mole. The ionization potential for trimethylsilane has not been previously reported. The ionization potential of 9.8 ± 0.3 ev is essentially the same as that of tetramethyl silicon, as might be expected and is in good agreement with the calculated value of 10.1 ev (see Table 8). The ionization potentials of the series of methyl substituted silanes might be expected on the basis of the equivalent-orbital treatment to fall into a series, where I_{SiH_4} I_{SiH_3Me} $I_{SiH_2Me_2}$ I_{SiHMe_3} I_{SiMe_4}.

Heats of Formation

The heats of formation for M^+, MCH_3^+, $M(CH_3)_2^+$, $M(CH_3)_3^+$, and $M(CH_4)_4^+$ are summarized in Table 9. The heats of formation for the ions where M = C indicate that carbon is unlike the remaining members of the family, Si, Ge, Sn, and Pb. Trends noted in the heats of formation for the ions formed from the group IV compounds include an apparent slight increase with increasing atomic number of the central atom for MMe_4^+, MMe_3^+, and MMe_2^+. The values for MMe^+ and M^+ do not show such trends and appear to stay fairly constant. The differences

Table 9. A Summary of the Heats of Formation for the Ions Studied.

	H_f^+				
M	MMe_4^+	MMe_3^+	MMe_2^+	MMe^+	M^+
C	208[a]	179[b]	231[a]	413[b]	395[a]
Si	163	166	194	235	278[a]
		146	201	218	300
Ge	177	168	226	245	279
Sn	177	183	225	253	276
Pb	217	206	236	223	251
Hg			158	160	257[a]

(a) See reference (9).
(b) See reference (28).

noted between neopentane and the other group IV tetramethyl compounds upon examining the heats of formation may be discussed further. Lampe and Field (28) in a study of the electron impact spectroscopy of neopentane indicate the formation of allyl and vinyl ions. While CCH_3^+ probably rearranges to $HC = CH_2^+$, this is not believed to be the case with MCH_3^+, where M = Si, Ge, Sn, and Pb. Many rearrangements are noted for the compounds studied, particularly trimethylsilane, but double bonds are not believed to be formed. Lampe and Field (28) found the complementary reactions

$$\underline{\text{neo}}\text{-}C_5H_{12} \longrightarrow CH_3^+ + \underline{t}\text{-}C_4H_9$$

and

$$\underline{\text{neo}}\text{-}C_5H_{12} \longrightarrow \underline{t}\text{-}C_4H_9^+ + CH_3$$

to occur in neopentane. These workers noted that such reactions are rather rare. The possibility of such reactions occurring with the molecules reported here must also be considered. Such reactions could conceivably occur in several cases, particularly with trimethylsilane, as the shape of the ionization efficiency curves in several cases indicate that two reactions are occurring. Use is made of the concept of complementary reactions in the case of m/e 15 and 27 for trimethylsilane to calculate the heats of formation of the radicals $SiH(CH_3)_2$ and/or $SiCH_3$, $SiHCH_3$, and $SiH(CH_3)_2$.

If $\Delta H_f(SiCH_3) = 73$ kcal/mole, (from Table 6) and $\Delta H_f^+(SiCH_3) = 218$ or 235 kcal/mole (see Table 9), the ionization potential of $SiCH_3$ is calculated to be either 6.3 or 7.0 ev. Alternatively, if $\Delta H_f(SiCH_3)$ is calculated using the relation

$$\Delta H_f(SiCH_3) = 3D(Me_3Si\text{-}Me) - 3\Delta H_f(Me) + \Delta H_f(SiMe_4) \qquad (9)$$

giving $\Delta H_f(SiCH_3) = 57$ kcal/mole, $I(SiCH_3)$ is calculated to be either 7.0 or 7.7 ev. The average value of 7.0 ± 0.4 ev is taken as the best value. From $\Delta H_f(SiHCH_3) = 21$ kcal/mole (Table 6) and $\Delta H_f^+(SiHCH_3) = 220$ kcal/mole (Table 6), $I(SiHCH_3) = 8.6$ ev. Similarly, with $\Delta H_f(SiHCH_3) = 25$ kcal/mole and $\Delta H_f^+(SiHMe_2) =$

188 kcal/mole, the ionization potential of $SiHMe_2$ is calculated to be 7.1 ev.

In a like manner, values of the ionization potentials of various radicals may be estimated using equations similar to equation 9. Employing the bond dissociation energies $D(Me_3Si{-}Me) = 72$ kcal/mole, $D(Et_3Ge{-}Et) = 51$ kcal/mole, $D(Et_3Sn{-}Et) = 54$ kcal/mole, $D(Et_3Pb{-}Et) = 31$ kcal/mole, $D(CH_3Hg{-}CH_3) = 51$ kcal/mole, and $D(H_3Si{-}H) = 75$ kcal/mole (18), given by Cottrell (5), approximate values of the ionization potentials of various radicals were calculated. The results of these calculations are shown in Tables 10 and 11.

Table 10. Derived Ionization Potentials of Silicon-containing Radicals.

No. Me	No. H				
	0	1	2	3	4
0	8.15[a]	8.4[a]		8.7[a]	12.3[a]
1	7.0 ± 0.4	8.6 ± 0.3	9.3 ± 0.3		
2	7.8 ± 0.3	7.1 ± 0.3			
3	7.8 ± 0.5	9.8 ± 0.3			
4	9.8 ± 0.15				

(a) See reference (9).

Table 11. Derived Ionization Potentials of the Organometallics and their Radicals.

M	MMe_4	MMe_3	MMe_2	MMe
Si	9.8 ± 0.15	7.8 ± 0.5	7.8 ± 0.3	7.0 ± 0.4
Ge	9.2 ± 0.2	8.0 ± 0.3	9.7 ± 0.3	9.7 ± 0.4
Sn	8.25 ± 0.15	7.6 ± 0.3	8.5 ± 0.3	8.7 ± 0.4
Pb	8.0 ± 0.4	7.5 ± 0.4	8.9 ± 0.5	8.4 ± 0.6
Hg			8.9 ± 0.2	8.2 ± 0.3

SUMMARY

A great deal of qualitative similarity exists between the mass spectra in this group of related compounds, particularly the group IV tetramethyl compounds. In each case the dominant species in the mass spectrum is the ion formed from the parent molecule minus a CH_3 group. A number of other interesting relationships are noted between the tetramethyl compounds of group IV, trimethylsilane and dimethyl mercury.

The processes for the formation of M^+, MCH_3^+, $M(CH_3)_2^+$, $M(CH_3)_3^+$, and $M(CH_3)_4^+$ for the tetramethyl compounds and for MCH_3^+ and $M(CH_3)_2^+$ for dimethyl mercury are all quite similar with the neutral fragments in each case being methyl groups. Trimethylsilane presents a somewhat different case. The formation of various hydrides necessitated the determination of appearance potentials of many more ions; the processes were confirmed by literature values of heats of formation and by comparison to heats of formation calculated for the ions of tetramethyl silicon. The energetics indicate the formation of C_2H_6, CH_4, and other neutral fragments in some cases in addition to CH_3.

The ionization potentials for tetramethyl germanium, tetramethyl lead, and the methyl substituted silanes, were calculated using a modified Hall equivalent orbital treatment. The parameters were calculated and interpolated from experimental ionization potentials of neopentane, tetramethyl silicon, and tetramethyl lead. Calculated values of 9.1, 7.8, and 10.1 ev compared quite favorably with experimental values of 9.2 ± 0.2 ev, 8.0 ± 0.4 ev, and 9.8 ± 0.3 ev for tetramethyl germanium, tetramethyl lead, and trimethylsilane, respectively.

Derived values for the ionization potentials of metal-containing radicals are tabulated.

The determination of electron impact spectroscopy data for this group of related compounds has provided much useful information about these organometallic compounds.

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REFERENCES

(1) Abel, E. W., G. Nickless, and F. H. Pollard, *Proc. Chem. Soc.*, *1960*, 288.

(2) Beynon, J. H., in "Advances in Mass Spectrometry," edited by J. D. Waldron, Pergamon Press, Inc. New York, 1959, p. 328.

(3) Beynon, J. H., "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, 1960, p. 53.

(4) Cameron, A. E. and D. F. Eggers, Jr., *Rev. Sci. Instr.*, *19*, 605 (1948).

(5) Cottrell, T. L., "The Strengths of Chemical Bonds", Butterworths Scientific Publications, London (1958).

(6) Dibeler, V. H. and R. L. Mohler, *J. Research Natl. Bur. Standards*, *47*, 337 (1951).

(7) Dibeler, V. H., *J. Research Natl. Bur. Standards*, *49*, 235 (1952).

(8) Elder, R. A., C. Giese, M. G. Inghram, and B. Steiner, "Ninth Annual Meeting, ASTM Committee E-14 on Mass Spectrometry", Chicago, Illinois, June, 1961.

(9) Field, F. H. and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press, Inc., New York. 1957.

(10) Franklin, J. L., *Ind. Eng. Chem.*, *41*, 1070 (1949).

(11) Franklin, J. L., *J. Chem. Phys.*, *22*, 1304 (1954).

(12) Fraser, R. G. J. and T. N. Jewitt, *Proc. Roy. Soc. (London)*, *A160*, 563 (1937).

(13) Friedman, L., A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, *77*, 3689 (1955).

(14) Gallegos, E. J. and R. W. Kiser, *J. Am. Chem. Soc.*, *83*, 773 (1961).

(15) Gohlke, R. S., *Anal. Chem.*, *31*, 535 (1959).

(16) Good, W. D., E. W. Scott, J. L. Lacina, and J. P. McCullough, *J. Phys. Chem.*, *63*, 1139 (1959).

(17) Gruttner, G., and E. Krause, *Ber. Dtsch. Chem. Ges.*, *50*, 1802 (1917).

(18) Gunn, S. R., and L. G. Green, *J. Phys. Chem.*, *65*, 779 (1961).

(19) Hall, G. G. and J. Lennard-Jones, Proc. Roy. Soc. (London), A202, 155 (1950).

(20) Hall, G. G. and J. Lennard-Jones, Proc. Roy. Soc. (London), A205, 357 (1951).

(21) Hall, G. G., Proc. Roy. Soc. (London), A205, 541 (1951).

(22) Hall, G. G., Trans. Faraday Soc., 49, 113 (1953).

(23) Hall, G. G., Trans. Faraday Soc., 50, 319 (1954).

(24) Harrington, D. B., "Advances in Mass Spectrometry" edited by J. D. Waldron, Pergamon Press, London, 1959, pp. 249-265.

(25) Katzenstein, H. S. and S. S. Friedland, Rev. Sci. Instr., 26, 324 (1955).

(26) Kaufman, J. J. and W. S. Koski, J. Am. Chem. Soc., 82, 3262 (1960).

(27) Kiser, R. W., "Tables of Ionization Potentials", U. S. Atomic Energy Commission, TID-6142, June 20, 1960.

(28) Lampe, F. W. and F. H. Field, J. Am. Chem. Soc., 81, 3238 (1959).

(29) Lennard-Jones, J., Proc. Roy. Soc. (London), A198, 1 (1949).

(30) Lennard-Jones, J. and J. A. Pople, Proc. Roy. Soc. (London), A202, 166 (1950).

(31) Lippincott, E. R. and M. C. Tobin, J. Am. Chem. Soc., 75, 4141 (1953).

(32) Long, L. H. and R. G. W. Norrish, Trans. Roy. Soc., London, A241, 587 (1949).

(33) Moore, C. E., "Atomic Energy Levels," Natl. Bur. Standards Circ. 467, Vol. III, 1958.

(34) Quinn, E. I., V. H. Dibeler, and F. L. Mohler, J. Research Natl. Bur. Standards, 57, 41 (1956).

(35) Rossini, R. D. and J. W. Knowlton, J. Chem. Phys., 6, 168 (1938).

(36) Rossini, R. D., D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(37) Stevenson, D. P., Discussions Faraday Soc., 10, 35 (1951).

(38) Streitwieser, Jr., A., J. Am. Chem. Soc., 82, 4123 (1960).

(39) Tanaka, Y., A. S. Jursa, and F. J. LeBlanc, J. Chem. Phys., 28, 350 (1958).

(40) Tannenbaum, S., S. Kaye, and G. F. Lewenz, J. Am. Chem. Soc., 75, 3753 (1953).

(41) Warren, J. W., Nature, 165, 811 (1950).

(42) Washburn, E. W., "International Critical Tables", McGraw-Hill Book Co., Inc., New York, 1929, Volume V, p. 163.

(43) Wiley, W. C., Science, 124, 817 (1956).

(44) Wiley, W. C., and I. H. McLaren, Rev. Sci. Instr., 26, 1150 (1955).

(45) Wolff, M. M. and W. E. Stephens, Rev. Sci. Instr., 24, 616 (1953).

ELECTRON IMPACT SPECTROSCOPY OF TETRAMETHYL -SILICON, -GERMANIUM, -TIN, AND -LEAD, TRIMETHYLSILANE AND DIMETHYL MERCURY

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AN ABSTRACT OF A THESIS

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An examination of the literature reveals that electron impact data for a large number of molecules has been reported. This important information is quite obviously lacking for nearly all of the organometallic compounds. The group IV tetra-alkyls and related organometallics are in most cases well suited to provide such data, and can provide useful information on structure and relative probabilities of bond dissociation processes within a group of such compounds. Therefore the electron impact spectroscopy of the group IV tetramethyl compounds, trimethylsilane, and dimethyl mercury were studied.

The mass spectra and appearance potentials reported here were obtained with a Bendix Model 12-100 time-of-flight mass spectrometer with an analog output system consisting of a monitor and scanner. Mass spectra were obtained at nominal electron energies of 70 ev. Appearance potentials were determined using the method of extrapolated difference described by Warren. Krypton or xenon mixed with the compound being investigated was used to calibrate the ionizing voltage.

Mass spectra for the group IV tetramethyl compounds were qualitatively similar, with the trimethyl ion being dominant in each case and the parent molecule-ions having an extremely low abundance. The mass spectra for trimethylsilane and dimethyl mercury were also similar in that in both of the latter compounds the dominant ion was formed by the parent minus a CH_3 group. Hydride formation was more apparent in the compounds with a central atom of lower atomic number.

The processes for the formation of the principal ions in the mass spectra of the group IV tetramethyl compounds and dimethyl mercury in each case appear to involve the stepwise formation of CH_3 groups as the neutral fragments. The energetics rule out the possibility of formation of ethane. Trimethylsilane presents a different case, however, as the energetics indicate the formation of methane and ethane as neutral fragments with certain ions.

The ionization potentials reported here, $SiMe_4$ = 9.8 ev, $GeMe_4$ = 9.2 ev, $SnMe_4$ = 8.25 ev, $PbMe_4$ = 8.0 ev, $HgMe_2$ = 8.9 ev, and $SiHMe_3$ = 9.8 ev are new; only a value of 11.5 ev for $PbMe_4$ had been reported previously. Calculations of ionization potentials for $SiHMe_3$, $GeMe_4$, and $PbMe_4$ using a modified Hall equivalent orbital treatment give values of 10.1 ev, 9.1 ev, and 7.8 ev, respectively, which are in good agreement with the values determined experimentally.