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A Thermochemical Study Of Three Chemical Systems By Mass Spectrometry

Leighton Leroy Coatsworth

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A THERMOCHEMICAL STUDY

OF

THREE CHEMICAL SYSTEMS BY MASS SPECTROMETRY

by

Leighton Leroy Coatsworth

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
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ABSTRACT

In the first part of this work the reaction of gaseous BF$_3$ with molten B$_2$O$_3$ in a molecular flow reactor was studied with a mass spectrometer. Over the temperature range 930 - 1300°K the reaction was found to produce B$_2$OF$_4$ with the stoichiometry

$$4\text{BF}_3(\text{g}) + \text{B}_2\text{O}_3(\text{l}) = 3\text{B}_2\text{OF}_4(\text{g})$$

From the temperature dependence of the equilibrium constant, the enthalpy change for this reaction was determined to be 18.5 ± 3 kcal/mole and $\Delta H^0_f(B_2OF_4)$ calculated to be $-454 \pm 2$ kcal/mole at 1100°K.

Secondly, a mass spectrometric study of tetramethyl-diphosphine was carried out. A fragmentation scheme for the parent ion was proposed based on mass spectral data, metastable transitions, and electron impact energetics. The thermal decomposition of $(\text{CH}_3)_2\text{P-P(}\text{CH}_3)_2$ was found to produce dimethylphosphino radicals at a reactor temperature of 1000°K. Appearance potential data indicated a lower limit of 69.6 ± 5 kcal/mole for the P-P bond dissociation energy in tetramethylidiphosphine.
In the third part, the metal-metal bonded series 
(CH₃)₃M-Mn(CO)₅ (M = Si, Ge, Sn, Pb) was studied in a mass spectrometer specially equipped to minimize thermal decomposition effects. Fragmentation pathways for parent ions were characterized by the study of metastable transitions and appearance potential measurements. Electron impact energetic data was used to calculate metal-metal bond dissociation energies of 57.0 ± 6.7, 62.5 ± 7.8, 54.7 ± 6.9, and 46.8 ± 11.8 kcal/mole for the silicon, germanium, tin, and lead compounds respectively.

The thermal decomposition of (CH₃)₃Sn-Mn(CO)₅ was investigated and a mechanism for the pyrolysis was proposed.
ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Dr. Dino R. Bidinosti for his patience, expert advice and guidance throughout the course of this work.

I also wish to thank my associate Dr. John R. Krause for many valuable discussions which have been beneficial in the conduct of this research and in the preparation of this manuscript.

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PART I

Mass Spectrometric Study

of the Reaction of

$\text{BF}_3(g)$ with $\text{B}_2\text{O}_3(l)$
INTRODUCTION

Thermodynamic investigations by mass spectrometry of high temperature inorganic systems have become one of the most powerful tools for the study of gas-solid or gas-liquid equilibria. Hundreds of gaseous molecules, many of which were unknown and unexpected, have been identified and their relevant thermodynamic quantities have been measured. An excellent comprehensive review on the subject has been recently published (1).

Basically the method consists of establishing an equilibrium between the condensed phase and the vapour in an enclosed crucible called a Knudsen or effusion cell. A molecular beam effusing from a pinhole in the cell is made to intersect an electron beam in the ionizing region of a mass spectrometer. The resulting ions are then mass analyzed. The ion current for a particular mass is proportional to the concentration of a particular molecular species in the beam and can be related to its partial pressure inside the effusion cell. By varying the temperature of the effusion cell and recording the ion currents owing to
the various species emerging from the cell at each temper-
atture, thermodynamic data can be obtained.

The primary advantages of this method in opposition to
other analytical techniques include usually unambiguous
identification of the effusing species along with the
capability of detecting components at very low relative
concentrations. Moreover, the only exit from the effusion
cell is so small that the effusing molecular flow leaves the
inside equilibrium essentially undisturbed.

The present study involved the reaction of gaseous
boron trifluoride with molten diboron trioxide over the
temperature range 930 - 1300\textdegree{}K in a molecular flow reactor.
Previous mass spectrometric studies (2, 3) of equilibria in
the B-O-F system at high temperatures have demonstrated the
existence of two reactions

\begin{align*}
\text{BF}_3(g) + \text{B}_2\text{O}_3(l) & = (\text{BOF})_3(g) & \text{[I-1]} \\
\text{and} \quad (\text{BOF})_3(g) & = 3\text{BOF}(g) & \text{[I-2]}
\end{align*}

Thermochemical data concerning the species BOF and (BOF)_3
have since been well documented (4).

In both of these studies the major fragment ion from
(BOF)_3 corresponded to a loss of BO_2 from the molecular ion,
and was postulated as arising from a ring opening and migra-
tion of a fluorine atom (2). The mass spectra of analogous compounds $\text{B}_3\text{O}_3\text{H}_3$ (5), $\text{B}_3\text{O}_3\text{H}_2\text{F}$ (6), $\text{B}_3\text{O}_3\text{HF}_2$ (6), $\text{B}_3\text{O}_3\text{Cl}_3$ (7), and $\text{B}_3\text{O}_3(\text{CH}_3)_3$ (8) have also been reported. For the first three of these the major fragment ion resulted from the loss of a hydrogen atom, while the major fragment ion from the last two resulted from the loss of a chlorine atom and a methyl group respectively. In the light of these results, the major fragment ion, $\text{B}_2\text{OF}_3^+$, from (BOF)$_3$ is completely unexpected.

However, by analogy with $\text{BF}_2^+$ from the mass spectrum of $\text{BF}_3$, the ion $\text{B}_2\text{OF}_3^+$ would be an expected ion in the mass spectrum of the unknown species $\text{B}_2\text{OF}_4$, and would probably be the principal ion from this compound. A recent study of the mass spectrum of the gaseous products produced from $\text{BF}_3$ vapour in a microwave discharge reactor made of quartz has resulted in the formation of the ion $\text{B}_2\text{OF}_4^+$ (9). These authors postulated the existence of the neutral parent molecule $\text{B}_2\text{OF}_4$ formed from the discharge.

The purpose of this re-examination of the reaction of $\text{BF}_3$ with molten $\text{B}_2\text{O}_3$ in a molecular flow reactor was to show the existence of $\text{B}_2\text{OF}_4$, establish the stoichiometry of the reaction, and determine the heat of the reaction from temperature dependence studies.
EXPERIMENTAL

The Mass Spectrometer

The mass spectrometer used in this study was designed and constructed in this laboratory. It is a single focusing, 90° sector magnetic field instrument having a radius of curvature of 38.2 cm. A schematic diagram of the essential features is given in Figure I-1. Because previous studies in this laboratory have included descriptions of the present instrument (10, 11), the instrumentation will be discussed only briefly. However, modifications incorporated into the mass spectrometer during this investigation will be considered in greater detail.

An assembly of components known as an ion source is responsible for the electron bombardment formation, electrostatic acceleration, and focusing of a positive ion beam. The central feature of this ion source is the sequential stacking of components onto four accurately located ceramic rods. An exploded view of the design used for this instrument is given in Figure I-2.
FIGURE 1-1
THE MASS SPECTROMETER
FIGURE 1-2

EXPLODED VIEW OF ION SOURCE ASSEMBLY
The foundation for this structure is the exit plate $S_2$. It is used to attach the complete ion source assembly to the entrance of the ion analyzer tube, as well as to position the object slit and to provide anchoring holes for the ceramic rods. Individual plates, fabricated from stainless steel, type 304, or from Inconel, are stacked on the ceramic rods and are electrically insulated from each other by quartz spacers. The assembled components of the ion source are held rigidly in place by four set-screw shaft collars.

End plate $S_1$ contains a 1.59 mm x 9.52 mm slit through which a gaseous sample is introduced in the form of a molecular beam. The sample is ionized by interaction with an electron beam obtained by heating a thin rhenium filament ribbon $F$, mounted adjacent to the ionization chamber $C$, with a direct current of approximately 2.5 amperes. Heating causes thermal emission of electrons which are accelerated towards the ionization chamber by a potential difference maintained between the filament and the chamber. This potential difference (i.e., the energy of the electron beam) is accurately monitored by a Simpson Model 2700 Digital Voltmeter.

The electron beam enters the ionization region through
a 1.32 mm diameter hole in the chamber wall at right angles to the sample gas stream. Once through the ionization region, the electron beam exits through another hole (4.57 mm diameter) in the opposite wall and is collected by a cylindrically shaped trap T.

Ions formed are continuously extracted from the chamber by a potential gradient which exists between the cage and the plate directly below it, D. The focusing and shaping of the ion beam and its ejection into the ion analyzer tube are accomplished by the remaining plates and slits. The potential difference between the cage and the grounded exit plate (containing the object slit) provides the acceleration potential for the ion beam.

The ions are separated into individual beams each with an unique mass-to-charge ratio by the magnetic analyzer according to the expression (12)

$$\frac{m}{e} = \frac{H^2 r^2}{2Ve^2} \quad [I-3]$$

where $m$ is the mass in atomic mass units

e is the number of electronic charges

$H$ is the magnetic field strength in gauss

$r$ is the radius of curvature in cm

$V$ is the ion accelerating potential in volts
and \( c \) is the velocity of light.

The focusing properties of a sector instrument are such that the image slit allows only one of the individual mass beams to pass through for a constant set of conditions. The success in separating the whole ion beam into its individual components is expressed as resolution. The resolving power is given by

\[
\frac{M}{\Delta M} = \frac{R}{w_o + w_i}
\]  

[I-4]

where \( \Delta M \) is the mass difference of two ions

\( w_o \) is the width of the object slit (0.102 mm)

\( w_i \) is the width of the image slit (0.312 mm)

and \( R \) is the radius of curvature (38.2 cm).

The calculated resolution is 920 and the actual resolution using the 10% valley definition (13) is 700.

By sweeping the magnetic field, ion beams of consecutive m/e values are made to pass through the image slit and are collected on the first dynode of a sixteen stage electron multiplier which has a gain factor of approximately \( 10^4 \).

The ion current so produced is measured by determining the potential drop across a high resistance (10^9 ohms) with a vibrating reed electrometer. The output signal of the electrometer is displayed on a strip chart recorder.
The identity of the m/e values of the various ionic species are ascertained by comparing measured magnetic field strength values against a computer generated table or by counting from known background peaks.

The chamber housing both the ion source and the molecular flow reactor used in this study was fabricated from stainless steel type 304, and is schematically illustrated in Figure I-3. The chamber is divided into two sections by a rimmed plate P. This divider contains a 6 mm x 6 mm beam passage orifice and guide grooves for movable shutter S. The shutter is a small flat rectangular plate having a 1.34 mm x 6.27 mm beam defining slit and is actuated externally by means of a bellows-sealed mechanism.

The ion source and reactor cell regions are pumped by an Edwards EM2 and a CVC MGH-180 mercury diffusion pump respectively. In order to ensure a high vacuum in the chamber, both of these pumps are fitted with vapour traps cooled with liquid nitrogen. Pressures in each region of the chamber were monitored with Bayard-Alpert type ionization gauges. During a typical run, pressures differed by at least an order of magnitude between each chamber region, indicating that differential pumping had been achieved.
FIGURE 1-3
ION SOURCE ARRANGEMENT WITH MOLECULAR FLOW REACTOR
The Molecular Flow Reactor

The molecular flow reactor used for this study is shown in Figure I-4. The reactor was made by drilling a 3.2 mm diameter hole in the center of the bottom of a Morganite cylindrical alumina crucible of 5 ml capacity. A snug fitting alumina tube was inserted until it penetrated $\frac{1}{4}$ of the interior length of the crucible, and then bonded to the exterior of the crucible base with Ceramabond 503 high temperature ceramic adhesive manufactured by Aremco Products Inc.. The top lip of the crucible was ground flat to accept a platinum foil cover containing the effusion orifice. This cover was held in place by a thin rim of ceramic adhesive applied after the foil was firmly pressed in place so that no adhesive was exposed to the reactants in the interior of the reactor. A platinum foil baffle was used to prevent direct line of sight transmission from the inlet tube to the effusion orifice. Tantalum heating wire was threaded back and forth through 41 alumina tubes, 3 cm long x 1.25 mm O.D., which were cemented about the circumference of the reactor. The alumina gas inlet tube projected 8 cm from the bottom of the reactor and was held in a stainless steel Swagelok fitting using teflon ferrules. This fitting was in turn welded to a Vacoa MV-25-XL precision gas metering valve
FIGURE 1-4

THE MOLECULAR FLOW REACTOR
located on the exterior of the main source flange.

A regulated constant current d.c. power supply, Hewlett-Packard Model 6439B, was used to heat the tantalum wire. With two radiation shields, B, (see Figure I-3) a cell temperature limit of 1350°C was imposed by the rate of energy transfer from the small diameter tantalum wire. Temperatures were measured with a pair of chromel-P/alumel thermocouples; one spot welded to the platinum top near its periphery and the second cemented to the base of the alumina reactor body. After full temperature equilibrium the maximum temperature difference recorded by the two thermocouples was at the highest temperature, where the reactor base was approximately 3°C hotter than the platinum top. During each run the temperature of each thermocouple, monitored on a dual channel Hewlett-Packard Model 7100B strip chart recorder, remained constant to within 1°C.

Procedure

Samples of B₂O₃ were prepared by decomposing Fisher reagent-grade boric acid in a platinum crucible over a Meker burner. The resulting oxide was fused at 650°C for 72 hours. After transfer to and assembly of the alumina
reactor, the B₂O₃ glass was further dehydrated by fusing under high vacuum in the mass spectrometer. The molten boric oxide presented a surface area of approximately 2 cm² to the vapour phase in the reactor.

Matheson C.P. grade BF₃ was vacuum distilled and passed through dry-ice acetone traps several times to remove any traces of HF. Approximately 2/3 atm. of purified BF₃ was transferred from the vacuum line to a one litre storage bulb equipped with a greaseless stopcock. The sample bulb was attached to the gas metering valve, and the BF₃ was used within 18 hours of purification.

Boron trifluoride is a very reactive compound (33). Consequently care was taken to ensure that the reactant BF₃ came into contact only with relatively inert materials. These materials were: 304 stainless steel, Kel-F, teflon, glass, and at high temperatures alumina and platinum.

Two basic criteria must be satisfied in order for a Knudsen type reactor to function properly: (i) flow through the effusion orifice must be molecular, and (ii) a condition of equilibrium must be established within the cell.

A condition of molecular flow exists when the rate of flow is limited not by collisions between molecules, but by collisions of molecules with the walls. In an effusion
reactor when \( P < \frac{0.027}{R} \) (29), where \( P \) is the pressure in torr and \( R \) is the radius of the orifice in millimeters, molecular flow exists. For the particular reactor used in this study, the limiting pressure is \( 6 \times 10^{-2} \) torr -- higher than the internal cell pressure as estimated in Appendix F.

To ensure that equilibrium has been established within the reactor, the probability of a given molecule leaving the cell through the orifice in a given time must be very small. This is accomplished by a high ratio of effective internal to orifice area. However, at temperatures used in this study, vapours in the cell and a condensed phase, molten \( \text{B}_2\text{O}_3 \), will constitute the equilibrium. In this case then, the surface area presented by the liquid boric oxide must be large compared to the orifice area; in fact the ratio is approximately 300:1.

The molecular flow reactor was heated to a temperature of \( 720°C \), and reactant \( \text{BF}_3 \) allowed to enter. After allowing sufficient time for thermal equilibrium to be established (about 30 minutes), the relative intensities of the resulting ions obtained on mass spectrometric analysis of the effusing vapours were determined. Identification of ions and hence their neutral progenitors was accomplished using: (i) mass
number, (ii) isotope ratios observed and calculated, (iii) shutter effect (21), and (iv) intensity variation as a function of pressure and temperature.

Appearance potentials were measured for most of the ions present using the extrapolated voltage difference method of Warren (17); the experimental details of which have been described previously (11). Mercury, present as background in the mass spectrometer due to the diffusion pumps, was used as the calibrant.

At a constant temperature of 720°C, the stoichiometry of the equilibrium processes occurring in the reactor were ascertained by observing appropriate ion intensities as a function of the pressure of BF₃. The pressure of BF₃ in the reactor was altered by adjusting the leak rate from the external reservoir using the gas metering valve.

Once the stoichiometry for an equilibrium process had been established, the flow of BF₃ into the reactor was allowed to reach a steady, convenient value. The appropriate ion intensities were then observed as a function of the reactor temperature. A period of approximately 20 minutes was allowed to expire between observations to ensure that the reactor and its contents had reached thermal equilibrium.
RESULTS AND DISCUSSION

The increase in volatility of $\text{B}_2\text{O}_3(1)$ during reaction with $\text{BF}_3(g)$ has been recognized for many years (22). Previous discussions (2, 3) on the nature of this reaction were based on the assumption that the volatile compounds trifluoroboroxine, $(\text{BOF})_3$, and fluoroboroxine, $\text{BOF}$, were the only stable products formed. The primary objective of this study was to establish the existence of the molecular species $\text{B}_2\text{OF}_4$ as another product of the reaction.

At a reactor temperature of $934^\circ\text{K}$, the mass spectrum of the effusing reaction mixture was carefully scanned in the region expected for the ion $\text{B}_2\text{OF}_4^+$. A reproduction of the spectrum in this region is shown in Figure I-5. Peaks labeled "BG" in the partially resolved doublets at nominal masses 112 and 113 are due to background impurities. The theoretical isotope abundances calculated for $\text{B}_2\text{OF}_4^+$ are listed in Table I-1 along with the observed intensities for the same masses. In addition, opening and closing the shutter had a very pronounced effect on the intensities of
FIGURE 1-5
ISOTOPE PEAKS FOR $B_2OF_4^+$
TABLE I-1

Isotope Peaks for $\text{B}_2\text{OF}_4^+$

<table>
<thead>
<tr>
<th>m/e</th>
<th>Calculated*</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>6.18</td>
<td>6.34</td>
</tr>
<tr>
<td>113</td>
<td>49.71</td>
<td>48.93</td>
</tr>
<tr>
<td>114</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

* Using the computer program described in Appendix D
these peaks. This evidence, then, supports the existence of the molecular species $\text{B}_2\text{OF}_4$, but does not rule out the possibility of the ion $\text{B}_2\text{OF}_4^+$ arising as an electron impact induced fragment of some other molecular species.

The mass spectrum of the effusing reaction mixture is given in Table I-2 along with values quoted in previous studies. As indicated, the ion intensity of $\text{B}_2\text{OF}_4^+$ is approximately 500 times smaller than that for $(\text{BOF})_3^+$. This is no doubt the reason why the two earlier studies did not observe it. In the related reaction of $\text{BCl}_3(g)$ with $\text{B}_2\text{O}_3(1)$ (7), the ion $(\text{BOCl})_4^+$ was observed. The mass region above $(\text{BOF})_3^+$ was carefully examined at high sensitivity, but no ions corresponding to $(\text{BOF})_n^+$ ($n = 4, 5$) could be detected.

Appearance potentials for the observed ions are given in Table I-3. For comparison the values reported by Hildenbrand et al. (3) are also presented together with the averaged electron impact values for $\text{BF}_3$ from the review by Svec (23) and the photoionization values for $\text{BF}_3$ by Dibeler and Liston (24). The values obtained in this work for $\text{BF}_3^+$ and $\text{BF}_2^+$ are in much closer accord with the existing data for $\text{BF}_3$ (23, 24) than those of Hildenbrand et al. With the exception of $\text{B}_3\text{O}_3\text{F}_2^+$, all of the appearance potentials measured in this study are lower than theirs. The exception-
TABLE I-2
Mass Spectral Data for the Reaction
$\text{B}_2\text{O}_3(1) + \text{BF}_3(g)$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Relative Ion Intensities$^a$</th>
<th>This Work$^b$ ($934^\circ\text{K}$)</th>
<th>Ref. (2)$^c$ ($1093^\circ\text{K}$)</th>
<th>Ref. (3)$^d$ ($1286^\circ\text{K}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{BOF})_3^+$</td>
<td>100.00</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{O}_3\text{F}_2^+$</td>
<td>6.63</td>
<td>9.6</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_2\text{OF}_4^+$</td>
<td>0.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{B}_2\text{OF}_3^+$</td>
<td>41.33</td>
<td>59.5</td>
<td>60.5</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_2\text{F}_2^+$</td>
<td>19.43</td>
<td>30.8</td>
<td>34.4</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_2\text{F}^+$</td>
<td>19.65</td>
<td>11.3</td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td>$\text{BF}_3^+$</td>
<td>109.21</td>
<td></td>
<td>59.9</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Refers to summation of all isotopic species

$^b$ 50 eV electrons

$^c$ 75 eV electrons

$^d$ Mass spectrum of vapour species above a $3\text{MgF}_2:\text{B}_2\text{O}_3$ mixture; 60-75 eV electrons
TABLE I-3

Appearance Potentials for Ions

Formed in the Reaction $\text{B}_2\text{O}_3(1) + \text{BF}_3(g)$

<table>
<thead>
<tr>
<th>Ion</th>
<th>This Work</th>
<th>Ref. (3)</th>
<th>Ref. (23)</th>
<th>Ref. (24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BF}_3^+$</td>
<td>15.87 ± 0.1</td>
<td>16.4</td>
<td>15.7</td>
<td>15.55</td>
</tr>
<tr>
<td>$\text{BF}_2^+$</td>
<td>16.33 ± 0.1</td>
<td>16.7</td>
<td>16.2</td>
<td>15.81</td>
</tr>
<tr>
<td>$(\text{BOF})_3^+$</td>
<td>13.91 ± 0.1</td>
<td></td>
<td></td>
<td>14.2</td>
</tr>
<tr>
<td>$\text{B}_2\text{OF}_3^+$</td>
<td>15.35 ± 0.1</td>
<td></td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_2\text{OF}_4^+$</td>
<td>14.12 ± 0.1</td>
<td>13.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{O}_3\text{F}_2^+$</td>
<td>16.15 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_2\text{F}_2^+$</td>
<td>16.60 ± 0.2</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
al case is most interesting since Hildenbrand et al. report a value for $\text{B}_3\text{O}_3\text{F}_2^+$ which is lower than the ionization potential of $(\text{BOF})_3$ from which $\text{B}_3\text{O}_3\text{F}_2^+$ arises by fragmentive ionization; a result which is most improbable. The relative lack of initial curvature in the ionization efficiency curve, and the low value for the $\text{B}_2\text{OF}_4^+$ potential confirms that it is due to a direct ionization of the molecular species $\text{B}_2\text{OF}_4$.

In addition, six metastables were observed in the mass spectrum. These were assigned to the transitions shown in Table I-4 using the computer program described in Appendix E. The appearance potential of the metastable having $m/e = 65.38$ was measured as $15.3 \text{ eV}$. An ion resulting from a metastable transition has been shown (25) to have the same appearance potential as the same ion formed by the normal ionization and dissociation process. This substantiates the earlier (2) assignment of $\text{B}_2\text{OF}_4^+$ as a fragment from $(\text{BOF})_3$ involving a ring opening and migration of a fluorine atom.

A credible equilibrium reaction for the production of $\text{B}_2\text{OF}_4$ from the reaction mixture in the molecular flow reactor is

$$4\text{BF}_3(g) + \text{B}_2\text{O}_3(l) = 3\text{B}_2\text{OF}_4(g)$$ [I-5]

for which the equilibrium constant is given as
TABLE I-4

Metastable Transitions Observed in
the Mass Spectrum of the Reaction $\text{B}_2\text{O}_3(1) + \text{BF}_3(g)$

<table>
<thead>
<tr>
<th>$m_1^+ \rightarrow m_2^+ + m_3$</th>
<th>Metastable Mass</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td>Assigned Transition</td>
<td></td>
</tr>
<tr>
<td>$138 \rightarrow 95 + 43$</td>
<td>65.38</td>
<td>65.40</td>
<td>$(\text{BOF})_3^+ \rightarrow \text{B}_2\text{OF}_3^+ + \text{BO}_2$</td>
<td></td>
</tr>
<tr>
<td>$137 \rightarrow 94 + 43$</td>
<td>64.55</td>
<td>64.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$68 \rightarrow 49 + 19$</td>
<td>35.33</td>
<td>35.31</td>
<td>$\text{BF}_3^+ \rightarrow \text{BF}_2^+ + \text{F}$</td>
<td></td>
</tr>
<tr>
<td>$67 \rightarrow 48 + 19$</td>
<td>34.40</td>
<td>34.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$92 \rightarrow 49 + 43$</td>
<td>26.11</td>
<td>26.10</td>
<td>$\text{B}_2\text{O}_2\text{F}_2^+ \rightarrow \text{BF}_2^+ + \text{BO}_2$</td>
<td></td>
</tr>
<tr>
<td>$91 \rightarrow 48 + 43$</td>
<td>25.34</td>
<td>25.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ K_P = \frac{P^3 \text{B}_2\text{OF}_4}{P^4 \text{BF}_3} \]  
[I-6]

Using the relation derived in Appendix B between observed ion intensities and partial pressures of molecular species in an effusion reactor, equation [I-6] may be rewritten as

\[ K_P = \frac{C^3 \text{B}_2\text{OF}_4 \cdot I^3 \text{B}_2\text{OF}_4^+ \cdot T^3}{C^4 \text{BF}_3 \cdot I^4 \cdot \text{BF}_3^+ \cdot T^4} \]  
[I-7]

At a constant temperature equation [I-7] reduces to

\[ K_P = \frac{I^3 \text{B}_2\text{OF}_4^+}{I^4 \text{BF}_3^+} \cdot C \]  
[I-8]

Rearranging, and in terms of logarithms equation [I-8] becomes

\[ \log I_{\text{BF}_3^+} = \frac{3}{4} \log I_{\text{B}_2\text{OF}_4^+} + \frac{1}{4} \log \left(\frac{C}{K_P}\right) \]  
[I-9]

At a reactor temperature of 990°K, and using ionizing electrons of 50 eV, ion intensities from (BOF)_3 and B_2OF_4 were measured as a function of the pressure of BF_3. These results are graphically illustrated in Figure I-6, with slopes from a least squares straight line analysis listed in the upper left corner. The slope of 3/4 for the logarithmic plot of the ion intensities of BF_3^+ versus B_2OF_4^+ confirms the
FIGURE 1-6

INTENSITY DEPENDENCE OF IONS FROM
(BOF)$_3$ AND $B_2OF_4$ ON BF$_3$ PRESSURE
AT A REACTOR TEMPERATURE OF 993°K
stoichiometry of equation [I-5]. Unity slopes for $\text{(BOF)}_3^+$ and $\text{B}_2\text{OF}_3^+$ confirms the assignments of previous workers (2).

The variation of the equilibrium constant with temperature is given by the van't Hoff equation (26)

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$  \hspace{1cm} \text{(I-10)}

Assuming $\Delta H$ is constant over a given temperature range, substituting equation [I-7] into equation [I-10] and integrating gives

$$\log \frac{I^3_{\text{B}_2\text{OF}_4^+}}{I^4_{\text{BF}_3^+} T} = \frac{-\Delta H}{2.303RT} + C$$  \hspace{1cm} \text{(I-11)}

where $C$ is a constant independent of temperature. If an equilibrium has been established within the reactor, then a plot of the left side of equation [I-11] versus $1/T$ should be linear, and the slope of the line may be used to calculate the enthalpy change for the reaction.

At 50 eV, van't Hoff plots of ion currents for three different reactor pressures are shown in Figure I-7. The straight lines, calculated by the method of least squares, gave slopes which yielded an average $\Delta H = 18.5 \pm 3$ kcal/mole for reaction [I-5].

At the conclusion of the temperature dependence study
FIGURE 1-7

VAN'T HOFF PLOTS FOR THE EQUILIBRIUM

\[ 4BF_3(g) + B_2O_3(l) = 3B_2O_4(g) \]
the molecular flow reactor was disassembled, and upon examination, boric oxide was found adhering to the walls and inside the top of the reactor. This indicated that during the course of the experiment (approximately 72 hours) chemical transport of B₂O₃ to the interior surfaces of the reactor was taking place. Hence the surface area of molten B₂O₃ to effusion orifice area ratio was continuously changing from an initial value of 300:1 to about 1500:1. In chronological sequence the \( \Delta H \) values obtained were 19.01, 16.67, and 19.65 kcal/mole. Since there was no effect on the van't Hoff plots due to changes in the surface area ratio, it can be concluded that a state of equilibrium had been attained within the reactor over the full range of internal conditions.

The enthalpy change for reaction [I-5] is related to the enthalpies of formation according to

\[
\Delta H = 3\Delta H_f^0(B_2OF_4) - 4\Delta H_f^0(BF_3) - \Delta H_f^0(B_2O_3) \quad [I-12]
\]

Assuming \( \Delta H \) to be constant over the temperature range studied, (with the average temperature as 1100\(^\circ\)K) then with the available data (4) for the heats of formation of BF₃ and B₂O₃, the heat of formation for B₂OF₄ is calculated to be \(-454 \pm 2\) kcal/mole.
When this work was submitted for publication (34), a referee pointed out that another possible reaction resulting in the formation of the species B₂OF₄ was

\[(\text{BOF})_3 + \text{BF}_3 = 3\text{B}_2\text{OF}_4\]  \hspace{1cm} \text{[I-13]}

The equilibrium constant for this reaction is given by

\[K_p = \frac{P^3 \text{B}_2\text{OF}_4}{P^3 \text{BF}_3 P (\text{BOF})_3}\] \hspace{1cm} \text{[I-14]}

Rewriting this equation in terms of ion intensities and logarithms at a constant temperature yields

\[\log I_{\text{B}_2\text{OF}_4^+} = \frac{1}{3} \log \{I (\text{BOF})_3^+ \cdot I_{\text{BF}_3^+}^3\} + \frac{1}{3} \log (K_p/C)\]  \hspace{1cm} \text{[I-15]}

Using experimental data already obtained (see Figure I-6), the pressure dependence plot for equation [I-15] is shown in Figure I-8. The slope of 1/3 for this logarithmic plot confirms the stoichiometry of reaction [I-13]. Unfortunately, the molecular flow reactor assembly had been dismantled before the possibility of reaction [I-13] became known.

However, the same mass spectrometric thermochemical techniques could probably be applied to reaction [I-13] as a confirmation for the value obtained in this study for the heat of formation of the molecular species B₂OF₄.
FIGURE 1-8
PRESSURE DEPENDENCE PLOT FOR THE REACTION
\((\text{BOF})_3 + BF_3 \rightarrow 3\text{B}_2\text{OF}_4\)
PART II

A Mass Spectrometric Study of Tetramethyldiphosphine
INTRODUCTION

Whereas the first compound containing a phosphorus-phosphorus bond, P₂I₄, was prepared over 150 years ago (35), it has been only recently that an interest in diphosphorus compounds has developed. A number of review articles summarizing synthetic approaches, characteristic reactions, and stereochemistry of various compounds involving the P-P linkage have been published (36, 37, 38). However, physical data concerning the P-P bond, even in very simple systems, is scarce. Apart from P₂ and P₄, the dissociation energy for a P-P bond has been determined in only three compounds: P₂H₄, P₂Cl₄, and P₂I₄. In every case the bond energy was calculated by utilizing electron impact values obtained from a mass spectrometric study.

In this laboratory mass spectrometric techniques have been very successful in the determination of metal-metal bond dissociation energies in Mn₂(CO)₁₀ and Co₂(CO)₈ (39, 40, 41), as well as [π-C₅H₅Fe(CO)₂]₂, [π-C₅H₅Ru(CO)₂]₂, [π-C₅H₅Mo(CO)₃]₂, and [π-C₅H₅W(CO)₃]₂ (42). In these
studies, the thermal decomposition of the dimeric species

\[ X_2 = 2X \]  \hspace{1cm} [II-1] 

was examined under equilibrium conditions in a molecular flow reactor, and in each case the monomeric free radical species was produced and detected. Enthalpy changes accompanying this type of equilibria were obtained by thermodynamic methods, providing an alternative method to the electron impact scheme (see Appendix A) for the determination of bond dissociation energies.

The object of this study was to examine the fragmentation of the simplest alkyldiphosphine, tetramethyldiphosphine, under electron bombardment, and also to examine the thermal decomposition of this compound in a molecular flow reactor in an effort to determine the P-P bond dissociation energy.
EXPERIMENTAL

Apparatus

The mass spectrometer described in Part I was used without modification for the study of \((\text{CH}_3)_2\text{P}-\text{P}(\text{CH}_3)_2\). The molecular flow reactor used was machined from a solid rod of stainless steel, type 304, and is shown in Figure II-1. It was provided with a snug fitting stainless steel cap which contained a 1.0 mm diameter effusion orifice having a knife edge profile. The interior dimensions of the reactor were 23.8 mm by 11.3 mm diameter, which gave a ratio of internal surface to effusion orifice of greater than 1300:1. The inlet tube was 31.5 mm long by 1.5 mm interior diameter. The reactor was held by a force fit onto a 3.3 mm O.D. stainless steel inlet tube ST, which passed through the mounting plate M and was joined to the main source flange by a stainless steel Swagelok fitting using teflon ferrules. The vapour flow to this fitting, and hence to the reactor, was controlled by a Vacoa MV-25-XL precision gas metering valve located on the exterior of the
main source flange. A folded baffle H made from a 9 mm by 35 mm long strip of stainless steel was placed inside the reactor to deflect incoming molecules and prevent direct line of sight transmission through the orifice.

Tantalum heating wire W was threaded back and forth through 16 alumina tubes, AT, 30 mm long by 1.25 mm O.D., situated in equally spaced holes drilled in the reactor wall about its circumference. A Hewlett-Packard 6439B constant-current power supply was used to heat the tantalum wire. With two radiation shields a cell temperature limit of 1100°K was imposed by the rate of energy transfer from the small diameter tantalum wire. Temperatures were measured with a pair of chromel P/alumel thermocouples, TC, spot welded to the reactor as shown in Figure II-1. After full temperature equilibrium, the maximum temperature difference recorded by the two thermocouples was at the highest temperature, where the reactor top was approximately 3° hotter than the bottom. During each run the temperature of each thermocouple remained constant to within 1°. The reactor was outgassed at 1000°K for 5 hours before any tetramethyl-diphosphine was introduced into the system.

The shutter S was used to distinguish between ion
current intensities from molecules in the effusing molecular beam and those from background molecules in the ion source region. All ion intensities reported herein have been corrected for contribution from background vapours.

Procedure

Tetramethylldiphosphine is a clear, colourless, pyrophoric liquid having a vapour pressure of about 8 torr at room temperature. The sample used in this study was obtained from Strem Chemicals Inc. and was purified by several trap-to-trap distillations in order to remove any traces of \((\text{CH}_3)_3\text{P}, (\text{CH}_3)_2\text{PH}, \text{and CH}_3\text{PH}_2\). The purity was confirmed by a proton NMR which showed only the triplet of peaks associated with \((\text{CH}_3)_2\text{P}-\text{P(\text{CH}_3)}_2\) (43). Approximately 2 ml of the pure diphosphine was placed in the sample reservoir which was a 100 ml Pyrex bulb on one arm of a greaseless teflon-plug stopcock. The other arm was directly connected to the precision metering valve. The stopcock and the connecting glass joints used viton O-rings for sealing.

With the reactor at room temperature, tetramethylldiphosphine was allowed to leak into the system and mass spectra recorded at an ionizing energy of 50 eV. Appearance potentials for the major ions produced by electron impact
were also measured with the reactor at room temperature.

If thermal pyrolysis of $(\text{CH}_3)_2\text{P}-\text{P}(\text{CH}_3)_2$ resulted in symmetric cleavage of the P-P bond, then a free radical species, $'\text{P}(\text{CH}_3)_2'$, would be produced. In order to confirm that this alkylphosphino radical was indeed being formed appropriate ion intensities were monitored as a function of the reactor temperature at an ionizing energy of 50 eV.

Data was then taken to allow a van't Hoff type plot to be made in an effort to determine the dissociation energy of the P-P bond.
RESULTS AND DISCUSSION

"Normal" fragment ions observed in mass spectra are generally considered to result from a sequence of consecutive unimolecular decomposition reactions of excited molecular-ions. The stepwise loss of neutral atoms or radical groups from excited molecular-ions by simple (single or multiple) bond cleavages permits a fragmentation scheme to be deduced. Structures for "normal" fragment ions may be inferred from this fragmentation scheme if the gas phase structure for the neutral parent molecule is known.

The presence of ions due to rearrangement processes makes the interpretation of mass spectra more complex because of the added pathways in competition with "normal" fragmentation. In cases where rearrangements are known to occur, or are likely to occur, any conclusions regarding a particular ion's structure should only be made with the benefit of data from metastable transitions and appearance potential measurements.

The major ions observed in the 50 eV mass spectrum of
tetramethyldiphosphine are given in Table II-1. Since it is well known that alkyl and fluoroalkyl phosphorus compounds exhibit ions due to rearrangement processes (44-48), it is not unreasonable to expect to observe similar ions in the mass spectrum of tetramethyldiphosphine. For this reason, the observed ions are represented by simple molecular formulae in order that no ionic structure (and hence fragmentation pathways) be implied.

The simple molecular formulae were determined by calculating every possible combination of 2 phosphorus atoms, 4 carbon atoms, and 12 hydrogen atoms which corresponded to the observed m/e values. After discarding illogical combinations by reason of improper valency requirements, it was found that a unique P-C-H combination existed for each observed mass in all but three cases.

For these exceptions (nominal masses 62, 75, and 76), the true identity of the ionic species present could readily be determined by accurate mass measurements at high resolution. However, calculations indicated that the resolving power necessary for the required separation at masses 75 and 76 exceeded that of the mass spectrometer used in this study, and hence the true composition of these peaks must
<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>122</td>
<td>$\text{C}<em>4\text{H}</em>{12}\text{P}_2^+$</td>
<td>85.00</td>
</tr>
<tr>
<td>107</td>
<td>$\text{C}_3\text{H}_9\text{P}_2^+$</td>
<td>100.00</td>
</tr>
<tr>
<td>92</td>
<td>$\text{C}_2\text{H}_6\text{P}_2^+$</td>
<td>3.00</td>
</tr>
<tr>
<td>91</td>
<td>$\text{C}_2\text{H}_5\text{P}_2^+$</td>
<td>7.50</td>
</tr>
<tr>
<td>79</td>
<td>$\text{CH}_5\text{P}_2^+$</td>
<td>36.88</td>
</tr>
<tr>
<td>77</td>
<td>$\text{CH}_3\text{P}_2^+$</td>
<td>7.75</td>
</tr>
<tr>
<td>76</td>
<td>$\text{C}_3\text{H}_9\text{P}^+/\text{CH}_2\text{P}_2^+$</td>
<td>6.25</td>
</tr>
<tr>
<td>75</td>
<td>$\text{C}_3\text{H}_8\text{P}^+/\text{CHP}_2^+$</td>
<td>15.75</td>
</tr>
<tr>
<td>73</td>
<td>$\text{C}_3\text{H}_6\text{P}^+$</td>
<td>5.88</td>
</tr>
<tr>
<td>63</td>
<td>$\text{HP}_2^+$</td>
<td>6.25</td>
</tr>
<tr>
<td>62</td>
<td>$\text{C}_2\text{H}_7\text{P}^+/\text{P}_2^+$</td>
<td>95.00</td>
</tr>
<tr>
<td>61</td>
<td>$\text{C}_2\text{H}_6\text{P}^+$</td>
<td>68.75</td>
</tr>
<tr>
<td>59</td>
<td>$\text{C}_2\text{H}_4\text{P}^+$</td>
<td>69.38</td>
</tr>
<tr>
<td>58</td>
<td>$\text{C}_2\text{H}_3\text{P}^+$</td>
<td>15.63</td>
</tr>
<tr>
<td>57</td>
<td>$\text{C}_2\text{H}_2\text{P}^+$</td>
<td>57.50</td>
</tr>
<tr>
<td>56</td>
<td>$\text{C}_2\text{HP}^+$</td>
<td>13.13</td>
</tr>
<tr>
<td>48</td>
<td>$\text{CH}_5\text{P}^+$</td>
<td>5.00</td>
</tr>
<tr>
<td>47</td>
<td>$\text{CH}_4\text{P}^+$</td>
<td>45.00</td>
</tr>
<tr>
<td>46</td>
<td>$\text{CH}_3\text{P}^+$</td>
<td>92.50</td>
</tr>
<tr>
<td>45</td>
<td>$\text{CH}_2\text{P}^+$</td>
<td>84.38</td>
</tr>
<tr>
<td>44</td>
<td>$\text{CHP}^+$</td>
<td>35.00</td>
</tr>
</tbody>
</table>
be determined by other means.

A reproduction of a slow careful scan over the region at nominal mass 62 is given in Figure II-2. On the low mass side of the peak at nominal mass 62 a definite "bump" can be observed. Calculations indicate that a resolving power of 775 is necessary to separate ions $P_2^+$ ($m/e = 61.947536$) and $C_2H_7P^+$ ($m/e = 62.027543$). It is clearly evident from Figure II-2 that the resolution of this instrument is sufficient to allow a partial separation of these two peaks. Moreover, using the expression derived in Appendix E, the mass of the "bump" was calculated to be 61.948. Hence, both $P_2^+$ and $C_2H_7P^+$ contribute to nominal mass 62, with approximately 95% of the observed intensity due to the latter species.

The measured appearance potentials are listed in Table II-2, and the observed metastables along with their assigned transitions are given in Table II-3. At least two separate determinations were made for each appearance potential listed, and the errors quoted represent variations in the results obtained. The metastable transitions were assigned using the computer program described in Appendix E.

The relative lack of initial curvature in the ionization efficiency curve, and the low value for the
FIGURE 11-2
PARTIALLY RESOLVED M/E=62 REGION
<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Appearance Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>122</td>
<td>P_2(CH_3)_4</td>
<td>7.76 ± 0.1</td>
</tr>
<tr>
<td>107</td>
<td>P_2(CH_3)_3</td>
<td>9.88 ± 0.1</td>
</tr>
<tr>
<td>92</td>
<td>C_2H_6P_2</td>
<td>9.56 ± 0.1</td>
</tr>
<tr>
<td>91</td>
<td>C_2H_5P_2</td>
<td>12.32 ± 0.1</td>
</tr>
<tr>
<td>79</td>
<td>CH_5P_2</td>
<td>12.68 ± 0.1</td>
</tr>
<tr>
<td>77</td>
<td>CH_3P_2</td>
<td>10.05 ± 0.1</td>
</tr>
<tr>
<td>76</td>
<td>P(CH_3)_3</td>
<td>8.73 ± 0.1</td>
</tr>
<tr>
<td>75</td>
<td>C_3H_8P</td>
<td>10.03 ± 0.1</td>
</tr>
<tr>
<td>62</td>
<td>P(CH_3)_2H</td>
<td>8.96 ± 0.1</td>
</tr>
<tr>
<td>61</td>
<td>P(CH_3)_2</td>
<td>11.77 ± 0.1</td>
</tr>
<tr>
<td>59</td>
<td>C_2H_4P</td>
<td>13.46 ± 0.2</td>
</tr>
<tr>
<td>58</td>
<td>C_2H_3P</td>
<td>11.90 ± 0.2</td>
</tr>
<tr>
<td>57</td>
<td>C_2H_2P</td>
<td>14.85 ± 0.2</td>
</tr>
<tr>
<td>56</td>
<td>C_2HP</td>
<td>14.13 ± 0.2</td>
</tr>
<tr>
<td>47</td>
<td>CH_4P</td>
<td>11.90 ± 0.2</td>
</tr>
<tr>
<td>46</td>
<td>CH_3P</td>
<td>11.27 ± 0.2</td>
</tr>
<tr>
<td>45</td>
<td>CH_2P</td>
<td>14.16 ± 0.2</td>
</tr>
<tr>
<td>$m_2^+ + m_3^+ + m_3^+$</td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------</td>
<td>------------</td>
</tr>
<tr>
<td>$122^+</td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ightarrow 107^+ + 15$ | 93.94    | 93.84      | $P_2(CH_3)_4^+ightarrow P_2(CH_3)_3^+ + CH_3$ |
| $107^+ightarrow 91^+ + 16$ | 77.38    | 77.39      | $P_2(CH_3)_3^+ightarrow C_2H_5P_2^+ + CH_4$ |
| $75^+ightarrow 74^+ + 1$ | 72.90    | 73.01      | $C_3H_6P^+ightarrow C_3H_7P^+ + H$ |
| $121^+ightarrow 93^+ + 28$ | 71.45    | 71.48      | $C_4H_11P_2^+ightarrow C_2H_9P_2^+ + C_2H_4$ |
| $107^+ightarrow 79^+ + 28$ | 58.33    | 58.33      | $P_2(CH_3)_3^+ightarrow CH_5P_2^+ + C_2H_4$ |
| $107^+ightarrow 73^+ + 34$ | 49.83    | 49.80      | $P_2(CH_3)_3^+ightarrow C_3H_6P^+ + PH_3$ |
| $122^+ightarrow 76^+ + 46$ | 47.40    | 47.34      | $P_2(CH_3)_4^+ightarrow P(CH_3)_3^+ + PCH_3$ |
| $122^+ightarrow 75^+ + 47$ | 46.19    | 46.11      | $P_2(CH_3)_4^+ightarrow C_3H_6P^+ + CH_4P$ |
| $91^+ightarrow 62^+ + 29$ | 42.24    | 42.24      | $C_2H_5P_2^+ightarrow P_2^+ + C_2H_5$ |
| $59^+ightarrow 45^+ + 14$ | 34.39    | 34.32      | $C_2H_4P^+ightarrow CH_2P^+ + CH_2$ |
| $62^+ightarrow 46^+ + 16$ | 34.07    | 34.13      | $P(CH_3)_2H^+ + PCH_3^+ + CH_4$ |</p>
potential of the ion \( \text{C}_4\text{H}_{12}\text{P}_2^+ \) confirms that it is due to direct ionization of the molecular species \((\text{CH}_3)_2\text{P}-\text{P}(\text{CH}_3)_2\). Whereas appearance potentials for "normal" fragment ions exhibit successive increases that parallel the stepwise loss of atoms or groups of atoms from the molecular-ion, it has been observed that the appearance potentials for rearrangement ions are relatively low (49, 50). In either case, for the general electron impact induced reaction

\[
\begin{align*}
\text{X}^+ & \rightarrow \text{Y}^+ + \text{neutral} \\
\text{II-2}
\end{align*}
\]

the appearance potential of the fragment ion \((\text{Y}^+)\) is always greater than that of its precursor ion \((\text{X}^+)\) (51).

If nominal mass 76 was attributed to the ionic species \(\text{CH}_2\text{P}_2^+\), then extensive fragmentation of the molecular-ion would be necessary for its production. Consequently, the corresponding appearance potential would exhibit a rather high value. Such is not the case, and therefore it may be concluded that the ionic species at \(m/e = 76\) is \(\text{C}_3\text{H}_9\text{P}^+\), which can be attributed to a rearrangement of the molecular-ion forming the trimethylphosphine ion. This conclusion is confirmed by the observation of the metastable ion at \(m/e = 47.40\). Similarly, nominal mass 75 can be attributed to the ionic species \(\text{C}_3\text{H}_8\text{P}^+\).
A proposed fragmentation scheme, consistent with the measured appearance potentials, is given in Figure II-3. Reactions that have been confirmed by observation of the appropriate metastable ion are labeled with an asterisk. Equivalent fragmentations observed in the mass spectrum of $(CH_3)_3P$ (44), and analogous fragmentations observed in the mass spectrum of $(CH_3)_2P-P(CF_3)_2$ are labeled "a" and "b" respectively.

It is apparent from this fragmentation scheme that the majority of the breakdown pathways for the molecular-ion involve rearrangement processes. A feature of rearrangements is intramolecular bond formation that is, by necessity, accompanied by bond breaking, and the two processes must be considered together. The course of events giving rise to a rearrangement can be qualitatively described in the following manner.

When a molecule is ionized in a mass spectrometer, energy transfer between reactant species is not possible, and only the internal energy acquired upon ionization is available to cause fragmentation. It is assumed that the internal energy of the molecular-ion is sufficient to overcome an energy of activation, thereby forming an activated
Proposed Fragmentation Scheme for Tetramethyldiphosphine

Figure II-3
complex or transition state (52). Furthermore, it has been pointed out (53) that the activation energies for rearrangement processes in ions are usually quite small as compared with those in neutral molecules. Since the atoms and bonds in an activated complex are usually considered to be rather labile, then it is reasonable to assume that the lowest activation energy for a rearrangement might correspond to the case where bond formation occurs partially or completely in advance of bond breaking. The formation step supplies energy for the breaking step, thus giving an energetically favourable situation.

Therefore, the propensity of compounds containing phosphorus atoms to exhibit rearrangements may be attributed to: (i) the presence of low energy vacant d-orbitals into which electron donation or excitation can occur, thus allowing bond formation to precede bond breaking, and (ii) the presence of lone pair electrons that may also participate in bond formation.

The thermal pyrolysis of tetramethyldiphosphine was carried out in the molecular flow reactor over a temperature range of 436°K to 996°K. A substantial increase in the ratio of the $\text{P(CH}_3)_2^+$/$\text{P}_2\text{(CH}_3)_4^+$ ion currents (at an ionizing energy
of 50 eV) was observed over this temperature range as illustrated in Figure II-4. At the same time, the ratio of the \( \text{P}_2(\text{CH}_3)_2^+ / \text{P}_2(\text{CH}_3)_3^+ \) ion currents and \( \text{P}(\text{CH}_3)_2^+ / \text{PCH}_3^+ \) ion currents remained essentially constant as shown in Table II-4. Furthermore, at reactor temperatures in the range 875\(^\circ\)K to 996\(^\circ\)K, the ion \( \text{P}(\text{CH}_3)_2^+ \) was observed at electron impact energies below the appearance potential of the same ion at room temperature.

A recent structure determination of \( \text{P}_2(\text{CH}_3)_4 \) in the gas phase has shown that the molecule exists as two identical dimethylphosphino groups linked together through a phosphorus-phosphorus bond (54). The observations of this pyrolysis study are consistent with the assumption of the symmetric cleavage of this \( \text{P-P} \) bond to produce the dimethylphosphino radical. The ionization potential of the \( \cdot \text{P}(\text{CH}_3)_2 \) radical was determined at a reactor temperature of 998 ± 2\(^\circ\)K during three different pyrolysis runs. In all, eight determinations were made yielding an average value of 8.75 eV with a standard deviation of 0.1 eV.

It has been pointed out in a review article (55) that thermochemical information concerning the dimethylphosphino radical, and in general all alkylphosphino radicals, is
FIGURE 11-4

THERMAL PYROLYSIS OF

\[(\text{CH}_3)_2\text{P}-\text{P(CH}_3)_2\]
TABLE II-4

Thermal Pyrolysis of (CH₃)₃P-P(CH₃)₂

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>( \frac{I_P(CH₃)₂^+}{I_P₂(CH₃)₄^+} )</th>
<th>( \frac{I_P₂(CH₃)₄^+}{I_P₂(CH₃)₃^+} )</th>
<th>( \frac{I_P(CH₃)₂^+}{I_PCH₃^+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>436</td>
<td>0.854</td>
<td>0.757</td>
<td>0.397</td>
</tr>
<tr>
<td>500</td>
<td>0.881</td>
<td>0.734</td>
<td>0.482</td>
</tr>
<tr>
<td>610</td>
<td>1.29</td>
<td>0.716</td>
<td>0.406</td>
</tr>
<tr>
<td>676</td>
<td>0.884</td>
<td>0.711</td>
<td>0.482</td>
</tr>
<tr>
<td>735</td>
<td>1.37</td>
<td>0.646</td>
<td>0.650</td>
</tr>
<tr>
<td>798</td>
<td>1.62</td>
<td>0.650</td>
<td>0.574</td>
</tr>
<tr>
<td>853</td>
<td>2.94</td>
<td>0.642</td>
<td>0.576</td>
</tr>
<tr>
<td>893</td>
<td>6.18</td>
<td>0.604</td>
<td>0.614</td>
</tr>
<tr>
<td>941</td>
<td>18.4</td>
<td>0.601</td>
<td>0.912</td>
</tr>
<tr>
<td>996</td>
<td>38.2</td>
<td>0.565</td>
<td>0.988</td>
</tr>
</tbody>
</table>
rather scarce. In order to compare the value obtained in
the present study with the only previous mass spectrometric
attempts at the determination of $I[(\text{CH}_3)_2\text{P}^+]$ (56, 58), it
will be necessary to briefly describe the methods used by
these workers.

In an electron impact study of trimethylphosphine (56),
Fischler and Halmann indirectly determined the ionization
potential of the dimethylphosphino radical, $I[(\text{CH}_3)_2\text{P}^+] =
9.1 \pm 0.2$ eV. This value was obtained by using the observed
appearance potential of the $(\text{CH}_3)_2\text{P}^+$ fragment ion in
conjunction with the mean dissociation energy for the P-C
bonds in trimethylphosphine obtained from thermochemical
measurements (57). However, the reliability of a determination
of this type is questionable since it is based on the implicit
assumption that the energy required to cleave one P-C bond
in trimethylphosphine to form the dimethylphosphino radical
is equal to one third of the total enthalpy required to
break all of the P-C bonds in $\text{P}((\text{CH}_3)_3$. Such a postulate is
known to be invalid for other molecules (60) including
Group V molecules, e.g. $\text{NH}_3$ and $\text{PH}_3$ (55). In addition, an
indirect determination must be considered to be less precise
than a direct determination since the latter involves only
a single experimental result. In the former case, the combination of two or more results has the effect of increasing the uncertainty in the final value.

In the second study (58), McAllister and Lossing made a direct measurement of the ionization potential of the dimethylphosphino radical produced from the thermal decomposition of tetramethyldiphosphine in a fused-silica capillary furnace (59). However, the very small yield of radicals obtained allowed only an approximate ionization potential, \( I[(\text{CH}_3)_2\text{P}'] \approx 8.3 \text{ eV} \), to be measured, and the authors made no estimate of the uncertainty involved.

In the present study the thermal decomposition of tetramethyldiphosphine resulted in an abundant yield of \((\text{CH}_3)_2\text{P}'\) radicals whose ionization potential was measured directly. Since the value obtained is consistent with the two previous estimates, and since it has a high degree of precision, it may be concluded that the value \( 8.75 \pm 0.1 \text{ eV} \) represents the energy required for the process

\[
*\text{P(}\text{CH}_3\text{)}_2 + \text{e} \rightarrow \text{P(}\text{CH}_3\text{)}_2^+ + 2\text{e}
\]  

[II-3]

The dissociation energy for the P-P bond can be estimated using the relation given in Appendix A if it is assumed that: (i) the value of \( 11.77 \pm 0.1 \text{ eV} \) represents the energy required to produce the ion \( \text{P(}\text{CH}_3\text{)}_2^+ \) according to
the process
\[ P_2(CH_3)_4 + e \rightarrow P(CH_3)_2^+ + \cdot P(CH_3)_2 + 2e \] [II-4]
and (ii) the ions produced in equations [II-3] and [II-4] are energetically the same. The algebraic difference between equations [II-4] and [II-3] is the dissociation
\[ P_2(CH_3)_4 \rightarrow 2 \cdot P(CH_3)_2 \] [II-5]
for which \( D(P-P) = 11.77 - 8.75 = 3.02 \pm 0.2 \text{ eV} = 69.6 \pm 5 \text{ kcal/mole}. \)

The measurement of any appearance potential assumes that the ion being studied is formed by one process. If there is more than one fragmentation route giving rise to the same ion then it is assumed that the measured appearance potential represents the process which requires the least amount of energy. Clearly then, the validity of bond strengths calculated from electron impact energetics depends on the correct assignment of the process involved in the threshold measurement.

In the present case the fragmentation scheme (Figure II-3) indicates that the ion \( P(CH_3)_2^+ \) may be formed from three different processes, one of which is given in equation [II-4]. This same ion may also be formed from the decomposition of the rearrangement ions according to the processes
\[ \text{P}_2(\text{CH}_3)_4 + e \rightarrow \text{P}(\text{CH}_3)_3^+ + \text{PCH}_3 + 2e \]

\[ \text{P}(\text{CH}_3)_2^+ + \text{CH}_3 \]  

\[ \text{P}_2(\text{CH}_3)_4 + e \rightarrow \text{P}(\text{CH}_3)_2^+ \text{H}^+ + \text{PC}_2\text{H}_5 + 2e \]

\[ \text{P}(\text{CH}_3)_2^+ + \text{H} \]  

[II-6]  

[II-7]

If it is assumed that all three of these processes contribute to the observed intensity of the \( \text{P}(\text{CH}_3)_2^+ \) ion, then the calculated P-P bond strength relies on the postulate that the process requiring the least amount of energy is given by equation [II-4].

Using the relation given in Appendix A and electron impact values given in a study on trimethylphosphine (61), the ionic bond energy \( D(\text{P}-\text{C}^+) = 3.1 \pm 0.4 \text{ eV} \) was calculated for the \( \text{P}(\text{CH}_3)_3^+ \) ion. The sum of this value and the observed appearance potential for the rearrangement ion \( \text{P}(\text{CH}_3)_3^+ \) then yields an estimate, \( 11.8 \pm 0.5 \text{ eV} \), for the energy required for process [II-6]. Similarly, using electron impact values from a study on dimethylphosphine (56) and the observed appearance potential for the ion \( \text{P}(\text{CH}_3)_2\text{H}^+ \), an estimate of \( 11.5 \pm 0.8 \text{ eV} \) was determined for the energy required for process [II-7].

From these results, it is not possible to correlate the observed appearance potential for the \( \text{P}(\text{CH}_3)_2^+ \) ion,
11.77 ± 0.1 eV, with either process [II-6] or [II-7]. Furthermore, the energy required for process [II-4] could also be in the same general range or possibly even higher. Consequently, the value 69.6 ± 5 kcal/mole can be viewed as a lower limit for the phosphorus-phosphorus bond energy in tetramethyldiphosphine.

It should also be pointed out that this P-P bond energy is in agreement with values obtained from mass spectrometric studies on P-P bond energies in other compounds as shown in Table II-5. In addition, the P-P bond strength increases with methyl substitution which is analogous with the increase in N-N bond strength between H₂N-NH₂ and (CH₃)₂N-N(CH₃)₂ (62).

For the dissociation as given in equation [II-5] the equilibrium constant is given by

\[
K_P = \frac{P^2 \cdot P(CH₃)₂}{P^2 P(CH₃)₄} \quad [II-8]
\]

Using the relation derived in Appendix B between observed ion intensities and partial pressures of molecular species in an effusion reactor, equation [II-8] may be written as

\[
K_P = \frac{C^2 \cdot P(CH₃)₂ \cdot I^2 \cdot P(CH₃)⁺}{C P(CH₃)₄ \cdot I P(CH₃)⁺ \cdot T^2} \quad [II-9]
\]
TABLE II-5

Some Phosphorus-Phosphorus Bond Energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>D(P-P)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{P-} \text{PH}_2$</td>
<td>61.2 ± 4</td>
<td>58</td>
</tr>
<tr>
<td>$\text{Cl}_2\text{P-} \text{PCl}_2$</td>
<td>58</td>
<td>63</td>
</tr>
<tr>
<td>$\text{I}_2\text{P-} \text{PI}_2$</td>
<td>73</td>
<td>64</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{P-} \text{P(} \text{CH}_3)_2$</td>
<td>69.6 ± 5</td>
<td>This work</td>
</tr>
</tbody>
</table>
which reduces to

\[ K_p = C \frac{I^2 \cdot P(CH_3)_2^+ T}{I_{P_2(CH_3)_4}^+} \]  \[\text{[II-10]}\]

The variation of the equilibrium constant with temperature is given by the van't Hoff equation [I-10]. Assuming \( \Delta H \) is constant over a given temperature range, substituting equation [II-10] into equation [I-10] and integrating gives

\[ \log \frac{I^2 \cdot P(CH_3)_2^+ T}{I_{P_2(CH_3)_4}^+} = \frac{-\Delta H}{2.303RT} + C' \]  \[\text{[II-11]}\]

where \( C' \) is a constant independent of temperature. If an equilibrium has been established within the reactor, a plot of the left side of equation [II-11] versus \( 1/T \) should be linear, and the slope of the line may be used to calculate the enthalpy change for the reaction.

At temperatures above 875\( ^0 \)K, and with an ionizing energy of 50 eV, both the ionization of the dimethylphosphino radical and the electron impact induced fragmentation of tetramethyldiphosphine contribute to the observed ion current of the \( P(CH_3)_2^+ \) species. However, proper use of equation [II-11] requires that the ion currents \( P(CH_3)_2^+ \) and \( P_2(CH_3)_4^+ \) be related exclusively to the partial pressures of
P(CH₃)₂ and P₂(CH₃)₄ respectively in the molecular flow reactor. This was accomplished by operating at an electron energy below 11.77 ± 0.1 eV, but above 8.75 ± 0.1 eV.

Over a temperature range of approximately 850 to 1100⁰K, van't Hoff plots of ion currents taken at 10.8 eV for five different reactor pressures were made. In every case the data exhibited an excessive amount of scatter which made it impossible to obtain any meaningful results. Therefore, it must be concluded that an equilibrium had not been established within the reactor, for reasons that are not understood.

The combination of electron impact and mass spectrometric thermochemical techniques used in this study for the determination of the P-P bond energy in tetramethyldiphosphine have not been as successful as similar studies on other compounds (11, 42). The major difficulty in this case arises because of the extensive rearrangements occurring upon electron bombardment. Indeed, this problem reflects a general problem in furthering this area of experimentation, namely, what compounds to study in order to obtain the maximum possible information about the bonding.

The compound (CF₃)₂P-P(CF₃)₂ might be more suitable for a study of this type, since the mass spectrum shows no peaks due to rearrangements (CF₃)₃P⁺ or (CF₃)₂PF⁺ (47).
addition, the symmetric cleavage of the P-P bond is supported by the appropriate metastable transition. Also, a study on another diphosphine, $\text{P}_2\text{F}_4$, would seem to be appropriate, since this compound has been shown to readily undergo thermal decomposition to form $^{1}\text{PF}_2$ radicals (65).
PART III

A Mass Spectrometric Study
of the Metal-Metal Bonded
Series \((\text{CH}_3)_3\text{M} \cdot \text{Mn(CO)}_5\)

\((\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb})\)
INTRODUCTION

Covalent metal-metal bonding in transition metal complexes has become widely recognized in the past decade and several reviews have appeared on the subject (66, 67, 68, 69, 71). The extensive interest in these compounds has resulted from the recognition that metal-metal bonds play a key role in the chemistry of large classes of compounds. In one such class, a transition metal is bonded to silicon, germanium, tin, or lead and it is with these complexes that the present work is concerned.

Although the first examples of compounds of this type were reported almost thirty years ago (72, 73), interest in these complexes did not develop until the discovery of stable \( \sigma \)-bonded alkyl derivatives of the transition metals (74, 75). It was quickly recognized (76) that stable organometallic complexes involving a hydrocarbon radical \( \sigma \)-bonded to a transition metal were formed only when the transition metal was simultaneously bonded to \( \pi \)-acceptor ligands such as carbon monoxide and/or cyclopentadienyl. This recognition made it logical that these same transition metals should be capable of forming similar \( \sigma \)-bonds with the other Group IVB elements.
Development of this field awaited the stimulus provided by the synthetic work of Gorsich (77). Since that time over 500 transition metal derivatives of Group IVB have been prepared and characterized, and several reviews are available which describe the general chemistry of these complexes (78, 79, 80, 81).

The main feature of interest in these compounds is the nature of the covalent metal-metal bond. Among the molecular parameters which are used to describe chemical bonds, perhaps one of the most fundamental is the concept of bond strength. Strictly interpreted, however, bond strengths can only have meaning when they are used in a comparative manner. For this reason, assessments of metal-metal bond strengths are usually carried out on series of closely related compounds. Organo-metallic compounds of the transition metal-Group IVB type are well suited for such studies since they often exist in series of molecules which differ from one another by systematic changes in a well defined variable. For example, the molecules $L_3M'-M(CO)_5$ ($L = Cl, Br, I, CH_3, C_2H_5, C_6H_5; M' = Si, Ge, Sn, Pb; M = Mn, Re$) may be divided into groups so that the effect on the strength of the metal-metal bond caused by changing the ligand, the Group IVB metal, or the Group VIIA metal may be investigated.
Infrared, nuclear magnetic resonance, nuclear quadrupole resonance, Mössbauer, and ultraviolet-visible spectroscopy as well as X-ray crystallography have all been used to investigate related series of transition metal-Group IVB compounds, and the results of these studies have been summarized in recent reviews (82, 83). These methods can, in principle, provide information regarding electron distributions, electronic energy levels and bond lengths. Consequently, it may be possible to correlate such information with metal-metal bond strengths. It should be pointed out however, that such indirect relations regarding metal-metal bond strengths are at best qualitative, and in the absence of other corroborating information they must be interpreted with caution (84, 85).

In addition, far infrared and Raman spectroscopy have been used to obtain metal-metal stretching frequencies of transition metal derivatives of Group IVB (86, 87, 88, 89, 90). In theory, the force constant for stretching the metal-metal bond should be a direct reflection of the metal-metal bond strength (91). In practice however, the metal-metal stretching mode is usually extensively coupled with other vibrational modes, and in order to obtain reliable force constants a complete vibrational analysis is necessary (82).
Such calculations are very complex, and only one series, $\text{Cl}_3\text{M'}\text{-Co(CO)}_4$ ($\text{M'} = \text{Si, Ge, Sn}$), has been treated in this manner (88).

The most direct measure of the strength of a chemical bond is the bond dissociation energy. If $A-B$ represents a molecule with a bond between fragments $A$ and $B$, then the bond dissociation energy is defined as the energy required for the process

$$A-B(g) \rightarrow A^*(g) + B^*(g)$$  \hspace{1cm} [III-1]

whereby one mole of the A-B bond is broken, with all species considered to be ideal gases at 0°K. Clearly then, the measurement of a bond dissociation energy yields a numerical quantity which gives an exact meaning to the concept of bond strength.

Although there are many methods for determining bond dissociation energies (60, 92, 93), electron impact techniques have become the most popular due to their relative simplicity and wide applicability. To date, however, mass spectrometric techniques have not been widely used to study the bonding in transition metal derivatives of Group IVB because of experimental difficulties arising from the behaviour of organo-metallic compounds in commercial mass spectrometers. It has been shown (96, 97) that thermal reactions in the inlet
system and/or the ion source of mass spectrometers can cause data interpretation problems as well as serious errors in appearance potential measurements. These difficulties are especially acute for highly volatile organometallic compounds (98, 42). In spite of these obstacles, a few mass spectrometric determinations of absolute metal-metal bond dissociation energies of transition metal derivatives of Group IVB have been obtained (94, 95).

The present study was conducted with two aims: (i) to develop techniques which would minimize the difficulties encountered with mass spectrometric studies of volatile organometallic compounds, and (ii) to use these techniques in an electron impact investigation of the effect of changing the Group IVB metal in the series \((\text{CH}_3)_3\text{Mn(CO)}_5\) (\(M = \text{Si, Ge, Sn, Pb}\)).
EXPERIMENTAL

It is perhaps worthwhile to precede any discussion of the experimental apparatus and the methods used in this work by emphasizing some of the main problems that may be encountered in mass spectrometric studies of organometallic systems.

Problems in the Mass Spectrometry of Organometallics

When fragmentation patterns of compounds containing polyisotopic metals are studied, the relative isotope abundances produce characteristic patterns which can be recognized, and therefore assist in the identification of metal-containing ion species. For organometallic compounds these patterns are the rule rather than the exception since only a few elements likely to be encountered are anisotopic or are at least nearly so. However, it is often the case that the presence of many isotopes yields very complicated patterns that are difficult to interpret, especially when isotope patterns overlap. This overlapping problem has been found to occur extensively in the mass spectra of metal hydrides (99).
Information concerning the mode of fragmentation is partly derived from an analysis of the metastable peaks observed in the mass spectrum. For ions containing poly-isotopic elements, the isotope abundance pattern will also appear in the observed metastable peak. Since metastables are usually broad, diffuse, low intensity species, the presence of an isotope pattern makes their observation and assignment extremely difficult (100), and in some cases impossible (101).

Some organometallic compounds are rather involatile at room temperature, and consequently they must be heated to sufficiently increase their vapour pressure in order that a mass spectrum may be obtained. Frequently, however, organometallic compounds are not thermally stable, and heating may cause appreciable thermal decomposition, thermal rearrangements, or polymerization (102, 103). Furthermore, in most mass spectrometers the bombarding electrons are produced by thermionic emission from an incandescent filament, and the heat generated from this hot filament is sufficient to cause an increase in the temperature of the surrounding metal parts of the ion source. It has been shown (96, 97, 98, 104, 105) that organometallic compounds in the gas phase may pyrolyze when in contact with these hot metal surfaces. The
resulting gaseous products or intermediates formed from such a pyrolysis will have almost the same probability for ionization as unreacted molecules. Hence, thermal reactions in the inlet system and/or ion source of mass spectrometers may produce products that contribute significantly to the mass spectrum, and therefore obscure that due to the molecule of interest. These thermal effects are difficult or impossible to either predict or detect in commercial instruments, since reactions which occur in the mass spectrometer may be more pronounced than expected from other experimental evidence (97, 106).

Perhaps one of the most serious problems encountered in the mass spectrometry of organometallic compounds occurs when a particular ion is formed not only from the dissociative ionization of the molecule of interest, but also from the ionization of pyrolysis products. Whenever more than one ionization process gives rise to the same ion, it is assumed that the measured appearance potential corresponds to that process which requires the least amount of energy. Clearly then, the validity of using appearance potential measurements for the derivation of bond dissociation energies will depend on the correct assignment of the process involved in the threshold measurement.
It should also be pointed out that the thermal decomposition of organometallic compounds almost always results in the deposition of thin metallic films on heated surfaces inside the mass spectrometer. These metal films may then act as catalysts for the decomposition of subsequent samples (96, 97, 98). Consequently, the authenticity of the mass spectra is dependent not only upon the temperature, but also on the condition of the ion source surfaces. Moreover, these deposited metal films eventually cause short circuits in the electrical connections resulting in the necessity for frequent cleaning of the entire ion source assembly (105).

The flow conditions in the ionization chamber of conventional mass spectrometers are such that sample molecules experience many wall collisions before being pumped away. Hence, even if sample molecules are not thermally induced to decompose or react, they may absorb enough thermal energy to populate higher vibrational and possible electronic levels. Ionization from these levels would then lead to completely different fragmentation patterns than those from unexcited molecules (108). In addition the population of these higher molecular energy states may lead to anomalously low values for appearance potentials (107, 109, 110).
Despite all of these obstacles, a number of mass spectrometric studies have been carried out on organometallic compounds and these have been recently summarized (111, 112). In most cases, the temperature of the ion source was kept as low as possible (approximately 40 to 150°C). A comparison of the mass spectra and appearance potentials reported, however, shows rather large discrepancies especially for very volatile compounds. These differences are no doubt due to thermal effects occurring in the inlet system and/or ion source region. In fact, it has recently been shown that even at an ion source temperature of 30°C, the compound HMn(CO)₅ shows considerable thermal decomposition (102).

The pyrolytic effects in the ion source have been essentially avoided by the use of two techniques: (i) a chopped molecular beam inlet system (113, 114), and (ii) photoionization (115, 116). In the first method, the sample is introduced into the ionization chamber in the form of a modulated molecular beam. The ions produced are then detected with a lock-in amplifier operating at the frequency of modulation. In this way, the measured ion current corresponds only to those molecules which have not experienced any collisions with the hot surfaces of the ion source. However, the apparatus involved in this method is
complex and expensive, and the sample molecules still decompose depositing thin metallic films in the ion source region. In the second method, the bombarding electron beam is replaced by a beam of photons. Although photoionization has the advantage of allowing the ion source region to remain at ambient temperature it is also very complex and extremely costly.

Measurements (42) have shown that the ionization chambers used in the mass spectrometers in this laboratory have an operating temperature of 150 ± 10°C. Therefore, in light of the above discussion, a cooled filament assembly was constructed in order to minimize the pyrolytic effects in the ion source region.

**Apparatus**

The mass spectrometer described in Part I and used in this study was modified to include: (i) a cooled filament assembly, and (ii) an automatic electron accelerating voltage scanning system.

A cut-away view of the cooled filament assembly showing construction details is given in Figure III-1. A series of interconnecting channels were machined into the copper block, B, in order to provide a continuous passage for a coolant
FIGURE iii-1
COOLED FILAMENT ASSEMBLY
gas. Two tubular ceramic insulators, T, brazed into the entrance and exit ports of this passageway, served both to introduce the cooling gas and to support the copper block. The filament, F, consisted of a rhenium ribbon (9.53 mm x 0.762 mm x 0.025 mm) spot welded to tungsten support rods, S, which were electrically isolated from the copper block by ceramic insulators, C. Connections for the necessary filament current were provided by the electrical feedthroughs, E. The electron beam entered the ionization chamber by passing through a 1.32 mm hole drilled in the top of the copper block. The complete ion source assembly including the cooled filament arrangement is shown in Figure III-2.

The temperature of the ionization chamber was monitored by an iron-constantan thermocouple spot welded onto the chamber wall adjacent to the copper block. The entire ionization chamber was cooled by circulating cold, dry, nitrogen gas (produced by the forced evaporation of liquid nitrogen) through the copper block. By adjusting the rate of gas flow, the chamber temperature, as displayed on an API Model 503 pyrometer, could be controlled to within ± 2°C over the range of -20 to 96°C.

Since one of the aims of this study was to obtain metal-metal bond dissociation energies by electron impact
methods, the second modification to the mass spectrometer was the addition of a semi-automatic device for obtaining ionization efficiency curves. The manual acquisition of these curves involves the measurement of ion currents corresponding to small steps (usually 0.1 eV) in the electron energy. This method is tedious and very time consuming with the added drawback that during the measurements the conditions in the ion source may change. In contrast, the device described below permits an entire, continuous curve to be obtained in less than two minutes.

The potential difference between the filament and the ionization chamber (i.e., the energy of the electron beam) is provided by a Kepco ABC-200M constant voltage power supply, and monitored with a digital voltmeter (DVM). A fifteen turn helipot (0.025% linearity) which acted as an external programming resistor was connected to this supply. The energy of the electron beam was scanned by turning this potentiometer with a Hurst Model AR-DA 1 rpm synchronous motor. By measuring the time taken for a one volt change as read from the DVM, the precise electron energy scanning rate was determined, and was found to be reproducible to within the accuracy of the DVM. A continuous ionization efficiency curve was obtained by scanning the electron energy
while simultaneously recording the corresponding ion current on a strip chart recorder.

Free-radical ionization potentials are of considerable importance in electron impact determinations of bond dissociation energies. In nearly all of the methods employed to date, radicals were formed by the thermal decomposition of a suitable compound, and were then ionized in a mass spectrometer. Although a large body of energetic data has been obtained for organic radicals, ionization potentials for organometallic radicals are almost unknown. This has been principally because of the lack of compounds that produce significant amounts of the desired organometallic radicals in thermal decomposition reactions. In order to ascertain whether radical species could be produced from the compounds used in this work under controlled thermal conditions, a molecular flow reactor was constructed.

The reactor consisted of an effusion cell and a surrounding copper block heater as shown in Figure III-3. The cell was constructed from a 60 mm long x 14 mm diameter quartz tube with one end containing a 0.79 mm diameter effusion orifice having a knife edge profile. The interior dimensions of the cell were such that the ratio of internal surface to effusion orifice area was approximately 4000:1.
The inlet tube, a 75 mm length of 3 mm diameter quartz tube attached to the bottom of the effusion cell, was held in a stainless steel Swagelok fitting using teflon ferrules. The vapour flow to this fitting, and hence to the cell, was controlled by a Nupro-2S metering valve located on the exterior of the main source flange. A triangular quartz baffle plate was fixed midway in the interior of the cell in order to deflect incoming molecules and to prevent direct line of sight transmission through the orifice.

The quartz cell was surrounded by a heater assembly which was machined from a 51 mm length of 25.4 mm diameter copper rod. Tantalum heating wire was threaded back and forth through ten alumina tubes situated in equally spaced holes drilled in the heater wall about its circumference. A Hewlett-Packard 6439B constant-current power supply was used to heat the tantalum wire. A cell temperature limit of 1100°K was imposed by the rate of energy transfer from the small diameter tantalum wire. Temperatures were measured with four chromel P/alumel thermocouples which were held in place next to the quartz cell with set screws as shown in Figure III-3. After full temperature equilibrium the maximum temperature difference recorded by the thermocouples was at the highest temperature, where the reactor base was approxi-
mately 4° hotter than the top. The entire assembly was outgassed at 1000°K for 5 hours before any samples were introduced into the system.

Procedure

All of the compounds studied in this work were low melting, highly volatile, air and light sensitive solids. They were each kept in sealed containers either under vacuum or under a nitrogen atmosphere and stored in a dark place until needed. In every case, the samples were repurified by sublimation immediately before being used.

A few crystals of the freshly sublimed material were placed in a 2 ml pyrex bulb on one arm of a greaseless teflon-plug stopcock. The other arm was connected directly to the Nupro metering valve of the sample introduction system as shown in Figure III-2. The vapour in the bulb, after passing through the low conductance valve, was introduced directly into the ionization chamber via a length of 3 mm diameter glass tubing which was long enough to reach the adapter in the top plate of the ion source but not long enough to obstruct the passage of electrons across the ionization chamber. The rate of flow of cold nitrogen gas passing through the copper block was adjusted until the ion source
temperature remained steady at approximately 20°C. The sample vapour was then allowed to leak into the system and mass spectra recorded at an ionizing energy of 50 eV. In addition, mass spectra were also taken with no cooling applied to the ion source in order to roughly ascertain the extent of thermal pyrolysis in the ionization chamber.

Since all four compounds studied in this work contained a polyisotopic Group IVB metal, each ion in the mass spectra of these compounds appeared as a discrete cluster of peaks having a characteristic isotope pattern. In order to compare the abundance of polyisotopic ions with other ions it was necessary to present mass spectra in terms of a single isotope. The most practical way of accomplishing this was to sum the intensity contributions of each isotope in a given cluster. This resulting sum was given the mass of the most abundant isotope in the cluster, and designated as a monoisotopic peak. In this work, the reduction of mass spectral data to monoisotopic form was carried out in the following manner.

Initially, the isotope pattern obtained for a particular ion was compared to a theoretical isotope pattern generated by the computer program given in Appendix D. If these two patterns agreed within experimental error, then the isotope intensities were summed. However, if there was a considerable
amount of disagreement, then it was assumed that the cluster in question corresponded to two or more superimposed patterns and these were then deconvoluted. Specific details, as well as an illustrative example of this deconvolution procedure is given in Appendix D. This procedure was repeated for each ion cluster until the entire mass spectrum was in mono-isotopic form. The most intense peak was designated the base peak and assigned a value of 100. Abundance values for all other ions in the mass spectrum were then expressed as percentages of the base peak.

Appearance potentials for most of the major ions produced by electron impact were evaluated from ionization efficiency curves using Warren's extrapolated voltage difference technique (17). Both calibrant (xenon) and sample ion curves were obtained with the electron energy scanning device and with an ion source temperature of 20°C. In order to reduce the time required for manual evaluation, and to eliminate any personal bias, the actual data analysis was performed by the computer program given in Appendix C.

One compound, Me₃Sn-Mn(CO)₅(Me = CH₃) was subjected to controlled thermal conditions in the quartz molecular flow reactor. If thermal pyrolysis resulted in the cleavage of the Sn-Mn bond, then Me₃Sn· and Mn(CO)₅ radical species
would be produced. In order to ascertain whether such radical species were being formed, appropriate 50 eV ion intensities as well as appearance potentials were monitored as a function of the reactor temperature.

**Materials**

Samples of $\text{Me}_3\text{M-Mn(CO)}_5$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) were provided by Dr. H.C. Clark's research group at this University. The preparation, isolation, and characterization of these compounds have been described in detail (89, 90), and will not be discussed here.

The preparation of trimethyllead manganesepentacarbonyl, $\text{Me}_3\text{Pb-Mn(CO)}_5$, was based on the method of Gorsich (77) using $\text{Me}_3\text{PbCl}$ and $\text{Mn}_2(\text{CO})_{10}$ as starting materials. Trimethyllead chloride was prepared as described by Heap and Summers (117), and dimanganese decacarbonyl was obtained from Strem Chemicals Inc..

A two-necked 100 ml round bottom flask, fitted with a nitrogen inlet and a magnetic stirring bar, was charged with 3 ml of clean dry mercury. Sodium metal (0.4 gm) was added in small pieces with stirring while maintaining a nitrogen atmosphere in the flask. When the resulting amalgam had cooled, $\text{Mn}_2(\text{CO})_{10}$ (1 gm) was added in 50 ml of tetrahydro-
furan which had been freshly distilled under nitrogen from potassium and benzophenone. The mixture was stirred for one hour under nitrogen with a magnetic stirrer and the resulting greenish-grey mixture was decanted into a second flask in a nitrogen filled glove bag. Trimethyllead chloride (1.5 gm) was added, the mixture was stirred for two hours, and left to stand overnight in a stoppered flask in the glove bag. Tetrahydrofuran was removed on a rotary evaporator and Me₃Pb-Mn(CO)₅ was separated from the light brown reaction residue by sublimation at room temperature onto a water cooled probe. During sublimation, the apparatus was not actively pumped on in order to prevent volatilization losses of Me₃Pb-Mn(CO)₅.

The resulting very pale yellow, cubic crystals of Me₃Pb-Mn(CO)₅ were mass spectroscopically pure, and the proton NMR was in excellent agreement with that obtained by Graham et al. (118). Since Me₃Pb-Mn(CO)₅ decomposes on exposure to light, it was kept under vacuum in a sealed container tightly wrapped in aluminum foil.
RESULTS AND DISCUSSION

Me₃SiMn(CO)₅

The sample of Me₃SiMn(CO)₅, initially in the form of very pale yellow crystals, gradually turned dark orange over a sixty hour period. Coincident with this colour change, the mass spectrum showed large increases in the relative intensities of the ions Me₃SiOSiMe₂⁺, Me₂SiOH⁺, HΜn(CO)₇⁺ (n = 1-5) and Mn(CO)₇⁺ (n = 0-5). Since (i) it has been shown (119) that Me₃SiMn(CO)₅ undergoes hydrolysis according to the reaction

\[2\text{Me}_3\text{SiMn(CO)}_5 + \text{H}_2\text{O} \rightarrow (\text{Me}_3\text{Si})_2\text{O} + 2\text{HMn(CO)}_5\]  [III-2]

(ii) Me₃SiOSiMe₂⁺ is the base peak in the mass spectrum of hexamethyldisiloxane (120), and (iii) Me₂SiOH⁺ is a commonly observed ion in methyl-silicon-oxygen compounds (121), it is reasonable to assume that Me₃SiMn(CO)₅ was reacting with trace amounts of water adsorbed on the surfaces of the mass spectrometer inlet system. Further evidence in support of this reaction was given by the appearance of a small peak due to (Me₃Si)₂O⁺ after the sample had been left attached to the inlet system for one week. A similar problem has been
encountered in obtaining the mass spectrum of the analogous compound Me$_3$SiCo(CO)$_4$ (95).

Because of the possible interference due to products of the hydrolysis reaction, no mass spectra were taken below m/e = 55, and all data reported for Me$_3$SiMn(CO)$_5$ in this work were taken within the first forty-eight hours of sample introduction. In addition, since it would be difficult to distinguish between hydrolysis products and thermal pyrolysis products, no mass spectra were taken without ion source cooling.

The monoisotopic, 50 eV, mass spectrum of Me$_3$SiMn(CO)$_5$ is given in Table III-1. Ions of the type Me$_3$SiMn(CO)$_n^+$ (n = 0-5) indicate that this compound is similar to most metal carbonyl derivatives in that one of the major fragmentation pathways involves the stepwise loss of all of the carbonyl groups before other bonds are broken. This breakdown scheme was confirmed by the observation of the appropriate metastable transitions as given in Table III-2. An equally prominent fragmentation pathway also occurs, namely, the initial loss of a methyl group followed by the stepwise loss of carbonyl groups giving ions of the type Me$_2$SiMn(CO)$_n^+$ (n = 0-5). Although no metastable was observed for the methyl group loss, all of the carbon monoxide losses were
### TABLE III-1

Mass Spectrum for $\text{Me}_3\text{SiMn(CO)}_5$

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>268</td>
<td>$\text{Me}_3\text{SiMn(CO)}_5^+$</td>
<td>28.20</td>
<td>169</td>
<td>$\text{Me}_2\text{SiMn(CO)}_2^+$</td>
<td>3.09</td>
</tr>
<tr>
<td>253</td>
<td>$\text{Me}_2\text{SiMn(CO)}_5^+$</td>
<td>6.88</td>
<td>168</td>
<td>$\text{HMn(CO)}_4^+$</td>
<td>0.25</td>
</tr>
<tr>
<td>240</td>
<td>$\text{Me}_3\text{SiMn(CO)}_4^+$</td>
<td>4.74</td>
<td>167</td>
<td>$\text{Mn(CO)}_4^+$</td>
<td>0.37</td>
</tr>
<tr>
<td>239</td>
<td>$\text{C}_3\text{H}_8\text{SiMn(CO)}_4^+$</td>
<td>0.12</td>
<td>156</td>
<td>$\text{Me}_3\text{SiMn(CO)}^+$</td>
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<tr>
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<td>155</td>
<td>$\text{C}_3\text{H}_8\text{SiMn(CO)}^+$</td>
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<tr>
<td>212</td>
<td>$\text{Me}_3\text{SiMn(CO)}_3^+$</td>
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<td>154</td>
<td>$\text{C}_3\text{H}_7\text{SiMn(CO)}^+$</td>
<td>0.13</td>
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<td>$\text{C}_3\text{H}_8\text{SiMn(CO)}_3^+$</td>
<td>0.25</td>
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<td>$\text{Me}_3\text{SiOSiMe}_2^+$</td>
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<td>$\text{Me}_2\text{SiMn(CO)}_3^+$</td>
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<td>$\text{HMn(CO)}_3^+$</td>
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<td>$\text{Mn(CO)}_5^+$</td>
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<td>$\text{Me}_2\text{SiMn}^+$</td>
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<tr>
<td>m/e</td>
<td>Ion</td>
<td>Relative Abundance</td>
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<tr>
<td>112</td>
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<tr>
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<td>H\text{Mn(CO)}^+</td>
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<td>83</td>
<td>Mn(CO)^+</td>
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<td>70</td>
<td>MeMn^+</td>
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<tr>
<td>55</td>
<td>Mn^+</td>
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<tr>
<td>$m_1 \rightarrow m_2 + m_3$</td>
<td>Metastable Mass</td>
<td>Assigned Transition</td>
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</tr>
<tr>
<td>268 $\rightarrow$ 240 + 28</td>
<td>214.96</td>
<td>214.93 $\text{Me}_3\text{SiMn(CO)}_5^+ \rightarrow \text{Me}_3\text{SiMn(CO)}_4^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>253 $\rightarrow$ 225 + 28</td>
<td>200.18</td>
<td>200.10 $\text{Me}_2\text{SiMn(CO)}_5^+ \rightarrow \text{Me}_2\text{SiMn(CO)}_4^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>240 $\rightarrow$ 212 + 28</td>
<td>187.29</td>
<td>187.27 $\text{Me}_3\text{SiMn(CO)}_4^+ \rightarrow \text{Me}_3\text{SiMn(CO)}_3^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>225 $\rightarrow$ 197 + 28</td>
<td>172.61</td>
<td>172.48 $\text{Me}_2\text{SiMn(CO)}_4^+ \rightarrow \text{Me}_2\text{SiMn(CO)}_3^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>212 $\rightarrow$ 184 + 28</td>
<td>159.73</td>
<td>159.70 $\text{Me}_3\text{SiMn(CO)}_3^+ \rightarrow \text{Me}_3\text{SiMn(CO)}_2^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>197 $\rightarrow$ 169 + 28</td>
<td>144.97</td>
<td>144.98 $\text{Me}_2\text{SiMn(CO)}_3^+ \rightarrow \text{Me}_2\text{SiMn(CO)}_2^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>184 $\rightarrow$ 156 + 28</td>
<td>132.24</td>
<td>132.26 $\text{Me}_3\text{SiMn(CO)}_2^+ \rightarrow \text{Me}_3\text{SiMn(CO)}^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>169 $\rightarrow$ 141 + 28</td>
<td>117.69</td>
<td>117.64 $\text{Me}_2\text{SiMn(CO)}_2^+ \rightarrow \text{Me}_2\text{SiMn(CO)}^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>156 $\rightarrow$ 128 + 28</td>
<td>105.06</td>
<td>105.03 $\text{Me}_3\text{SiMn(CO)}^+ \rightarrow \text{Me}_3\text{SiMn}^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>141 $\rightarrow$ 113 + 28</td>
<td>90.52</td>
<td>90.56 $\text{Me}_2\text{SiMn(CO)}^+ \rightarrow \text{Me}_2\text{SiMn}^+ + \text{CO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128 $\rightarrow$ 73 + 55</td>
<td>41.73</td>
<td>41.63 $\text{Me}_3\text{SiMn}^+ \rightarrow \text{Me}_3\text{Si}^+ + \text{Mn}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>83 $\rightarrow$ 55 + 28</td>
<td>36.45</td>
<td>36.45 $\text{Mn(CO)}^+ \rightarrow \text{Mn}^+ + \text{CO}\text{SiMn}^+ \rightarrow \text{Mn}^+ + \text{Si}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73 $\rightarrow$ 45 + 28</td>
<td>27.77</td>
<td>27.74 $\text{Me}_3\text{Si}^+ \rightarrow \text{MeSiH}_2^+ + \text{C}_2\text{H}_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>113 $\rightarrow$ 55 + 58</td>
<td>26.75</td>
<td>26.77 $\text{Me}_2\text{SiMn}^+ \rightarrow \text{Mn}^+ + \text{Me}_2\text{Si}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128 $\rightarrow$ 55 + 73</td>
<td>23.82</td>
<td>23.63 $\text{Me}_3\text{SiMn}^+ \rightarrow \text{Mn}^+ + \text{Me}_3\text{Si}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>268 $\rightarrow$ 73 + 195</td>
<td>19.91</td>
<td>19.88 $\text{Me}_3\text{SiMn(CO)}_5^+ \rightarrow \text{Me}_3\text{Si}^+ + \cdot\text{Mn(CO)}_5$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
supported by metastable transitions. This initial methyl group cleavage has been previously observed in the mass spectrum of an analogous compound \( \pi-C_5H_5(CO)_3MoSnMe_3 \) (101).

Relatively weak ions \( C_3H_7SiMn(CO)_{n+}^+ \) (\( n = 0-4 \)) and \( C_3H_7SiMn(CO)_{n}^+ \) (\( n = 0-3 \)) were observed due to hydrogen losses from the methyl groups attached to the silicon atom. In contrast, no ions were found due to the scission of carbon-oxygen bonds in the carbonyl ligands attached to the manganese atom.

Only one definite rearrangement ion, \( MeMn^+ \), was observed. A similar type of rearrangement ion (\( C_6H_5Mn^+ \)) has been observed in the mass spectrum of an analogous compound \( (C_6H_5)_3SnMn(CO)_5 \) (134).

The base peak in the mass spectrum of \( Me_3SiMn(CO)_5 \) was \( Me_3Si^+ \) which could arise from hydrolysis reaction products as well as from the dissociative ionization of the compound itself. However, a comparison of the mass spectral data obtained in this study with that previously recorded for hexamethyldisiloxane (120) indicated that no more than 1% of the observed intensity for \( Me_3Si^+ \) was due to fragmentation of \( (Me_3Si)_2O \).

The appearance potentials for the major ions that were not overlapped with other ions are given in Table III-3.
TABLE III-3

Appearance Potentials for Me₃SiMn(CO)₅

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Appearance Potential (eV)</th>
<th>Determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>268</td>
<td>Me₃SiMn(CO)⁺⁵</td>
<td>8.38 ± 0.15</td>
<td>14</td>
</tr>
<tr>
<td>253</td>
<td>Me₂SiMn(CO)⁺⁵</td>
<td>10.90 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>240</td>
<td>Me₃SiMn(CO)⁺⁴</td>
<td>9.56 ± 0.05</td>
<td>2</td>
</tr>
<tr>
<td>225</td>
<td>Me₂SiMn(CO)⁺⁴</td>
<td>12.62 ± 0.11</td>
<td>2</td>
</tr>
<tr>
<td>212</td>
<td>Me₃SiMn(CO)⁺³</td>
<td>10.49 ± 0.01</td>
<td>2</td>
</tr>
<tr>
<td>184</td>
<td>Me₃SiMn(CO)⁺²</td>
<td>11.21 ± 0.05</td>
<td>2</td>
</tr>
<tr>
<td>156</td>
<td>Me₃SiMn(CO)⁺</td>
<td>12.08 ± 0.16</td>
<td>2</td>
</tr>
<tr>
<td>73</td>
<td>Me₃Si⁺</td>
<td>9.78 ± 0.11</td>
<td>18</td>
</tr>
<tr>
<td>70</td>
<td>MeMn⁺</td>
<td>13.07 ± 0.16</td>
<td>2</td>
</tr>
<tr>
<td>55</td>
<td>Mn⁺</td>
<td>17.11 ± 0.52</td>
<td>2</td>
</tr>
</tbody>
</table>
The quoted values represent averages of the individual determinations, and the errors represent the standard deviations of these averages (122). In order to ensure that the ionization potential for \( \text{Me}_3\text{SiMn(CO)}_5^+ \) and the appearance potential for \( \text{Me}_3\text{Si}^+ \) were reliable values, more measurements were carried out for these two ions than for the other ions in the spectrum.

Since the observed appearance potential for \( \text{Me}_3\text{Si}^+ \), 9.78 ± 0.11 eV, is lower than appearance potentials of the same ion formed from any of the possible hydrolysis products (120), it may be concluded that \( \text{Me}_3\text{Si}^+ \) was formed according to the process

\[
\text{Me}_3\text{SiMn(CO)}_5 + e \rightarrow \text{Me}_3\text{Si}^+ + \cdot\text{Mn(CO)}_5 + 2e \quad [\text{III-3}]
\]

Furthermore, the metastable at \( m/e = 19.91 \) indicates that process [III-3] does indeed occur. Also, since the ionization potential for the trimethylsilyl radical has been measured by Lappert et al. (123) as 7.31 ± 0.18 eV, it is therefore possible to calculate the silicon–manganese bond dissociation energy in \( \text{Me}_3\text{SiMn(CO)}_5 \) by using equation [A-4]. This equation, for this compound, becomes

\[
D(\text{Me}_3\text{Si-Mn(CO)}_5) = A(\text{Me}_3\text{Si}^+) - I(\text{Me}_3\text{Si}.) \quad [\text{III-4}]
\]

for which \( D(\text{Si-Mn}) = 9.78 - 7.31 = 2.47 \pm 0.29 \text{ eV} = 57.0 \pm \)
6.7 kcal/mole.

Similarly, for the silicon-manganese ionic bond dissociation energy in Me₃SiMn(CO)⁺₅, equation [A-5] becomes

\[ D(\text{Me₃Si-Mn(CO)}⁺₅) = A(\text{Me₃Si}⁺) - I(\text{Me₃SiMn(CO)}₅) \]  \[ \text{[III-5]} \]

for which \( D(\text{Si-Mn}⁺) = 9.78 - 8.38 = 1.40 \pm 0.26 \text{ eV} = 32.2 \pm 6.0 \text{ kcal/mole}. \)

\text{Me₃GeMn(CO)}₅

The monoisotopic, 50 eV, mass spectrum of Me₃GeMn(CO)₅ is given in Table III-4. The ions Me₃GeMn(CO)⁺₅ and Me₂GeMn(CO)⁺ₕ (n = 0-5) along with the metastable transitions given in Table III-5 indicate that the major fragmentation pathway involves the initial loss of a methyl group followed by stepwise carbonyl losses.

The bracketed ion pairs listed in Table III-4 indicate situations where there is a possibility of two different ions contributing to the same nominal mass. In these cases, the true identity of the ionic species present could be determined by accurate mass measurements under high resolution conditions. Unfortunately however, the resolving power necessary for such measurements exceeded that of the mass spectrometer used in this study.
<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>314</td>
<td>Me$_3$GeMn(CO)$_5^+$</td>
<td>20.81</td>
</tr>
<tr>
<td>299</td>
<td>Me$_2$GeMn(CO)$_5^+$</td>
<td>7.47</td>
</tr>
<tr>
<td>286</td>
<td>{Me$_3$GeMn(CO)$_4^+$}</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>H$_2$MeGeMn(CO)$_5^+$</td>
<td></td>
</tr>
<tr>
<td>285</td>
<td>{C$_3$H$_8$GeMn(CO)$_2^+$}</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>HMeGeMn(CO)$_5^+$</td>
<td></td>
</tr>
<tr>
<td>271</td>
<td>Me$_2$GeMn(CO)$_4^+$</td>
<td>13.36</td>
</tr>
<tr>
<td>258</td>
<td>{Me$_3$GeMn(CO)$_3^+$}</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>H$_2$MeGeMn(CO)$_4^+$</td>
<td></td>
</tr>
<tr>
<td>257</td>
<td>{C$_3$H$_8$GeMn(CO)$_3^+$}</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>HMeGeMn(CO)$_4^+$</td>
<td></td>
</tr>
<tr>
<td>256</td>
<td>{C$_3$H$_7$GeMn(CO)$_4^+$}</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>MeGeMn(CO)$_4^+$</td>
<td></td>
</tr>
<tr>
<td>255</td>
<td>{C$_3$H$_6$GeMn(CO)$_3^+$}</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>CH$_2$GeMn(CO)$_4^+$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>243</td>
<td>Me$_2$GeMn(CO)$_3^+$</td>
<td>8.12</td>
</tr>
<tr>
<td>230</td>
<td>{Me$_3$GeMn(CO)$_2^+$}</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>H$_2$MeGeMn(CO)$_3^+$</td>
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</tr>
<tr>
<td>229</td>
<td>{C$_3$H$_8$GeMn(CO)$_2^+$}</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>HMeGeMn(CO)$_3^+$</td>
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</tr>
<tr>
<td>228</td>
<td>{C$_3$H$_7$GeMn(CO)$_3^+$}</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>MeGeMn(CO)$_3^+$</td>
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<td>227</td>
<td>{C$_3$H$_6$GeMn(CO)$_3^+$}</td>
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<tr>
<td></td>
<td>CH$_2$GeMn(CO)$_3^+$</td>
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</tr>
<tr>
<td>215</td>
<td>Me$_2$GeMn(CO)$_2^+$</td>
<td>5.16</td>
</tr>
<tr>
<td>202</td>
<td>{Me$_3$GeMn(CO)$_2^+$}</td>
<td>1.44</td>
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<tr>
<td></td>
<td>H$_2$MeGeMn(CO)$_2^+$</td>
<td></td>
</tr>
<tr>
<td>201</td>
<td>{C$_3$H$_8$GeMn(CO)$_2^+$}</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>HMeGeMn(CO)$_2^+$</td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td>Relative Abundance</td>
<td>m/e</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------</td>
<td>-----</td>
</tr>
<tr>
<td>( C_{3}H_{7}\text{GeMn}(CO)^+ )</td>
<td>0.22</td>
<td>130</td>
</tr>
<tr>
<td>Mn(CO)(_5^+)</td>
<td>6.36</td>
<td>129</td>
</tr>
<tr>
<td>Me(_2\text{GeMn}(CO)^+)</td>
<td>2.98</td>
<td>119</td>
</tr>
<tr>
<td>Me(_3\text{GeMn}^+)</td>
<td>19.87</td>
<td>111</td>
</tr>
<tr>
<td>Mn(CO)(_4^+)</td>
<td>14.06</td>
<td>104</td>
</tr>
<tr>
<td>Me(_2\text{GeMn}^+)</td>
<td>4.92</td>
<td>91</td>
</tr>
<tr>
<td>C(_2\text{H}_5\text{GeMn}^+)</td>
<td>2.87</td>
<td>90</td>
</tr>
<tr>
<td>C(_2\text{H}_4\text{GeMn}^+)</td>
<td>0.31</td>
<td>89</td>
</tr>
<tr>
<td>HMeGeMn(^+)</td>
<td>0.75</td>
<td>83</td>
</tr>
<tr>
<td>MeGeMn(^+)</td>
<td>5.38</td>
<td>75</td>
</tr>
<tr>
<td>CH(_2\text{GeMn}^+)</td>
<td>2.98</td>
<td>74</td>
</tr>
<tr>
<td>CHGeMn(^+)</td>
<td>3.62</td>
<td>70</td>
</tr>
<tr>
<td>Mn(CO)(_3^+)</td>
<td>12.78</td>
<td>55</td>
</tr>
</tbody>
</table>
## TABLE III-5

Metastables for $\text{Me}_3\text{GeMn(CO)}_5$

<table>
<thead>
<tr>
<th>$m_1^+ \rightarrow m_2^+ + m_3$</th>
<th>Metastable Mass</th>
<th>Assigned Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td>299 $\rightarrow$ 271 + 28</td>
<td>245.59</td>
<td>245.62</td>
</tr>
<tr>
<td>271 $\rightarrow$ 243 + 28</td>
<td>218.00</td>
<td>217.89</td>
</tr>
<tr>
<td>243 $\rightarrow$ 215 + 28</td>
<td>190.27</td>
<td>190.23</td>
</tr>
<tr>
<td>215 $\rightarrow$ 187 + 28</td>
<td>162.61</td>
<td>162.65</td>
</tr>
<tr>
<td>195 $\rightarrow$ 167 + 28</td>
<td>143.13</td>
<td>143.02</td>
</tr>
<tr>
<td>173 $\rightarrow$ 143 + 30</td>
<td>118.64</td>
<td>118.20</td>
</tr>
<tr>
<td>167 $\rightarrow$ 139 + 28</td>
<td>115.77</td>
<td>115.69</td>
</tr>
<tr>
<td>139 $\rightarrow$ 111 + 28</td>
<td>88.76</td>
<td>88.64</td>
</tr>
<tr>
<td>174 $\rightarrow$ 119 + 55</td>
<td>81.46</td>
<td>81.39</td>
</tr>
<tr>
<td>119 $\rightarrow$ 91 + 28</td>
<td>69.74</td>
<td>69.59</td>
</tr>
<tr>
<td>314 $\rightarrow$ 119 + 195</td>
<td>45.22</td>
<td>45.10</td>
</tr>
<tr>
<td>83 $\rightarrow$ 55 + 28</td>
<td>36.56</td>
<td>36.45</td>
</tr>
</tbody>
</table>
It should be pointed out that: (i) the ion pairs always occurred adjacent to one another, (ii) they had very small intensities compared to other ions in the spectrum, and (iii) although the individual ions of a pair could not be unambiguously identified, the pairs themselves could be separated by the deconvolution procedure of Appendix D. In this respect, the mass spectrum of Me₃GeMn(CO)₅ was unlike that of the analogous silicon compound where no such groups of ambiguous ion pairs were observed.

Although many ions were observed due to the rupture and/or rearrangement of hydrogens from the methyl groups attached to the germanium atom, no ions were found due to carbon-oxygen bond cleavage in the carbonyl groups attached to the manganese atom.

In common with the silicon analog, the rearrangement ion MeMn⁺ was observed in the mass spectrum of Me₃GeMn(CO)₅.

Ions containing only one metal atom corresponded to 74% of the total ion current when the ion source was cooled (14°C), and 75% when the ion source was not cooled (101°C). Hence, it may be assumed that very little, if any, thermal pyrolysis of Me₃GeMn(CO)₅ was occurring at the higher temperature.
The appearance potentials for the major ions that were not overlapped with other ions are given in Table III-6. The values listed are internally consistent with the exception of \( A(\text{Mn(CO)}_5^+) \) and \( A(\text{Mn(CO)}_4^+) \) which were abnormally high. The ionization efficiency curves for these two ions had long tails extending for approximately six volts, indicating that they were formed by very complex ionization processes. Furthermore, one cannot rule out the possibility that these ions were incorrectly assigned.

The low value of the appearance potential of \( \text{Me}_3\text{Ge}^+ \) and the observation of the metastable at \( m/e = 45.22 \) indicate that the ion \( \text{Me}_3\text{Ge}^+ \) was formed according to the process

\[
\text{Me}_3\text{GeMn(CO)}_5 + e \rightarrow \text{Me}_3\text{Ge}^+ + \cdot\text{Mn(CO)}_5 + 2e \quad \text{[III-6]}
\]

Using the reported \((123)\) value for the ionization potential of the trimethylgermamy radical, \( 7.11 \pm 0.18 \text{ eV} \), and equation \([A-4]\), the germanium-manganese bond dissociation energy in \( \text{Me}_3\text{GeMn(CO)}_5 \) is given by

\[
D(\text{Me}_3\text{Ge-Mn(CO)}_5) = A(\text{Me}_3\text{Ge}^+) - I(\text{Me}_3\text{Ge}^-) \quad \text{[III-7]}
\]

for which \( D(\text{Ge-Mn}) = 9.74 - 7.11 = 2.63 \pm 0.34 \text{ eV} = 62.5 \pm 7.8 \text{ kcal/mole.} \)

Similarly, using equation \([A-5]\), the germanium-manganese ionic bond dissociation energy in \( \text{Me}_3\text{GeMn(CO)}_5^+ \)
<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Appearance Potential (eV)</th>
<th>Determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>314</td>
<td>$\text{Me}_3\text{GeMn(CO)}_5^+$</td>
<td>8.32 ± 0.17</td>
<td>10</td>
</tr>
<tr>
<td>299</td>
<td>$\text{Me}_2\text{GeMn(CO)}_5^+$</td>
<td>11.07 ± 0.08</td>
<td>2</td>
</tr>
<tr>
<td>271</td>
<td>$\text{Me}_2\text{GeMn(CO)}_4^+$</td>
<td>12.71 ± 0.07</td>
<td>2</td>
</tr>
<tr>
<td>243</td>
<td>$\text{Me}_2\text{GeMn(CO)}_3^+$</td>
<td>13.60 ± 0.13</td>
<td>2</td>
</tr>
<tr>
<td>215</td>
<td>$\text{Me}_2\text{GeMn(CO)}_2^+$</td>
<td>14.51 ± 0.06</td>
<td>2</td>
</tr>
<tr>
<td>195</td>
<td>$\text{Mn(CO)}_5^+$</td>
<td>23.81 ± 0.43</td>
<td>2</td>
</tr>
<tr>
<td>187</td>
<td>$\text{Me}_2\text{GeMn(CO)}^+$</td>
<td>16.03 ± 0.09</td>
<td>2</td>
</tr>
<tr>
<td>174</td>
<td>$\text{Me}_3\text{GeMn}^+$</td>
<td>13.37 ± 0.11</td>
<td>2</td>
</tr>
<tr>
<td>167</td>
<td>$\text{Mn(CO)}_4^+$</td>
<td>23.52 ± 0.07</td>
<td>2</td>
</tr>
<tr>
<td>119</td>
<td>$\text{Me}_3\text{Ge}^+$</td>
<td>9.74 ± 0.16</td>
<td>12</td>
</tr>
<tr>
<td>83</td>
<td>$\text{Mn(CO)}^+$</td>
<td>20.06 ± 0.45</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>$\text{MeMn}^+$</td>
<td>18.00 ± 0.11</td>
<td>2</td>
</tr>
<tr>
<td>55</td>
<td>Mn$^+$</td>
<td>19.26 ± 0.16</td>
<td>2</td>
</tr>
</tbody>
</table>
is given by

\[ D(\text{Me}_3\text{Ge-Mn(CO)}_5^+) = A(\text{Me}_3\text{Ge}^+) - I(\text{Me}_3\text{GeMn(CO)}_5^+) \]  \hspace{1cm} \text{[III-8]}

for which \( D(\text{Ge-Mn}^+) = 9.74 - 8.32 = 1.42 \pm 0.33 \) eV = 32.7 ± 7.6 kcal/mole.

\text{Me}_3\text{SnMn(CO)}_5

The 50 eV monoisotopic mass spectrum of \text{Me}_3\text{SnMn(CO)}_5, Table III-7, was very much like that of its germanium analog. Again the fragmentation scheme displayed the parent ion \text{Me}_3\text{SnMn(CO)}_5^+ and ions \text{Me}_2\text{SnMn(CO)}_n^+ (m = 0-5) representing the initial loss of a methyl group followed by carbonyl losses. However, unlike the silicon and germanium spectra, the mass spectrum of \text{Me}_3\text{SnMn(CO)}_5 exhibits a metastable transition, Table III-8, for this initial methyl group loss.

Similar to the germanium analog, the spectrum of \text{Me}_3\text{SnMn(CO)}_5 contains possible ion pairs of the type \text{C}_3\text{H}_m\text{SnMn(CO)}_n^+ and \text{C}_m\text{H}_{4-n}\text{SnMn(CO)}_n+ (m = 6-9; n = 1-4) having the same nominal mass, and whose true identity cannot be readily determined.

Many ions were observed due to hydrogen loss and/or rearrangement from the methyl groups attached to the tin atom, but no ions were found due to carbon-oxygen bond cleavage in the carbonyl groups attached to the manganese
<table>
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<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
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<td>360</td>
<td>Me₃SnMn(CO)⁺₅</td>
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<td>345</td>
<td>Me₂SnMn(CO)⁺₅</td>
<td>64.49</td>
</tr>
<tr>
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</tr>
<tr>
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<td>{C₃H₈SnMn(CO)⁺₄, HMeSnMn(CO)⁺₅}</td>
<td>0.17</td>
</tr>
<tr>
<td>330</td>
<td>{C₃H₇SnMn(CO)⁺₄, MeSnMn(CO)⁺₅}</td>
<td>0.03</td>
</tr>
<tr>
<td>317</td>
<td>Me₂SnMn(CO)⁺₄</td>
<td>62.28</td>
</tr>
<tr>
<td>304</td>
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</tr>
<tr>
<td>302</td>
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</tr>
<tr>
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<td>Me₂SnMn(CO)⁺₃</td>
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</tr>
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</tr>
<tr>
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<td>C₃H₇SnMn(CO)⁺₂, MeSnMn(CO)⁺₃</td>
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<tr>
<td>261</td>
<td>Me₂SnMn(CO)⁺₂</td>
<td>17.16</td>
</tr>
<tr>
<td>248</td>
<td>Me₃SnMn(CO)⁺, H₂MeSnMn(CO)⁺₂</td>
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</tr>
<tr>
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<td>C₃H₈SnMn(CO)⁺, HMeSnMn(CO)⁺₂</td>
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</tr>
<tr>
<td>246</td>
<td>C₃H₇SnMn(CO)⁺, MeSnMn(CO)⁺₂</td>
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</tr>
<tr>
<td>233</td>
<td>Me₂SnMn(CO)⁺</td>
<td>8.34</td>
</tr>
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<td>Ion</td>
<td>Relative Abundance</td>
</tr>
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<td>Me₃SnMn⁺</td>
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<tr>
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<td>C₂H₄SnMn⁺</td>
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<td>190</td>
<td>MeSnMn⁺</td>
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<td>189</td>
<td>CH₂SnMn⁺</td>
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<tr>
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<td>CH₃SnMn⁺</td>
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<td>175</td>
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<td>165</td>
<td>Me₃Sn⁺</td>
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<td>Me₂Sn⁺</td>
<td>4.01</td>
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<tr>
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<td>MeSn⁺</td>
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<tr>
<td>120</td>
<td>Sn⁺</td>
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<tr>
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<td>Mn(CO)⁺</td>
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</tr>
<tr>
<td>70</td>
<td>MeMn⁺</td>
<td>12.97</td>
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<td>Mn⁺</td>
<td>20.29</td>
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<td>$m_1^+ - m_2^+ + m_3$</td>
<td>Metastable Mass</td>
<td>Assigned Transition</td>
</tr>
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<td>-----------------</td>
<td>---------------------</td>
</tr>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td>360 → 345 + 15</td>
<td>330.65</td>
<td>330.62</td>
</tr>
<tr>
<td>345 → 317 + 28</td>
<td>291.26</td>
<td>291.27</td>
</tr>
<tr>
<td>317 → 289 + 28</td>
<td>263.52</td>
<td>263.47</td>
</tr>
<tr>
<td>289 → 261 + 28</td>
<td>235.71</td>
<td>235.71</td>
</tr>
<tr>
<td>205 → 189 + 16</td>
<td>174.26</td>
<td>174.25</td>
</tr>
<tr>
<td>220 → 165 + 55</td>
<td>123.91</td>
<td>123.75</td>
</tr>
<tr>
<td>360 → 165 + 195</td>
<td>75.65</td>
<td>75.62</td>
</tr>
</tbody>
</table>
atom.

In common with both the silicon and germanium analogs the rearrangement ion MeMn\(^+\) was observed in the mass spectrum of Me\(_3\)SnMn(CO)\(_5\).

Ions containing only one metal atom corresponded to 32\% of the total ion current when the ion source was cooled (23\(^\circ\)C), and 35\% of the total when the ion source was not cooled (98\(^\circ\)C). Hence, it may be assumed that slight thermal pyrolysis of Me\(_3\)SnMn(CO)\(_5\) was occurring at the higher temperature.

The appearance potentials for the major ions that were not overlapped with other ions are given in Table III-9. The low value of the appearance potential of Me\(_3\)Sn\(^+\) and the observation of the metastable at m/e = 75.65 indicate that the ion Me\(_3\)Sn\(^+\) was formed according to the process

\[
\text{Me}_3\text{SnMn(CO)}_5 + e \rightarrow \text{Me}_3\text{Sn}^+ + \cdot\text{Mn(CO)}_5 + 2e \quad [\text{III-9}]
\]

Using the reported (123) value for the ionization potential of the trimethylstanyl radical, 6.93 ± 0.26 eV, and equation [A-4], the tin-manganese bond dissociation energy in Me\(_3\)SnMn(CO)\(_5\) is given by

\[
D(\text{Me}_3\text{Sn-Mn(CO)}_5) = A(\text{Me}_3\text{Sn}^+) - I(\text{Me}_3\text{Sn}^-) \quad [\text{III-10}]
\]
TABLE III-9

Appearance Potentials for Me₃SnMn(CO)₅

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Appearance Potential (eV)</th>
<th>Determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>Me₃SnMn(CO)₅⁺</td>
<td>8.30 ± 0.05</td>
<td>8</td>
</tr>
<tr>
<td>345</td>
<td>Me₂SnMn(CO)₅⁺</td>
<td>9.32 ± 0.03</td>
<td>2</td>
</tr>
<tr>
<td>317</td>
<td>Me₂SnMn(CO)₄⁺</td>
<td>11.69 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>289</td>
<td>Me₂SnMn(CO)₃⁺</td>
<td>12.78 ± 0.01</td>
<td>2</td>
</tr>
<tr>
<td>261</td>
<td>Me₂SnMn(CO)₂⁺</td>
<td>13.47 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>233</td>
<td>Me₂SnMn(CO)⁺</td>
<td>14.46 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>205</td>
<td>Me₂SnMn⁺</td>
<td>15.42 ± 0.03</td>
<td>2</td>
</tr>
<tr>
<td>190</td>
<td>MeSnMn⁺</td>
<td>18.22 ± 0.13</td>
<td>2</td>
</tr>
<tr>
<td>175</td>
<td>SnMn⁺</td>
<td>21.63 ± 0.03</td>
<td>2</td>
</tr>
<tr>
<td>165</td>
<td>Me₃Sn⁺</td>
<td>9.30 ± 0.04</td>
<td>10</td>
</tr>
<tr>
<td>150</td>
<td>Me₂Sn⁺</td>
<td>13.63 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>135</td>
<td>MeSn⁺</td>
<td>15.43 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>120</td>
<td>Sn⁺</td>
<td>14.23 ± 0.06</td>
<td>2</td>
</tr>
<tr>
<td>111</td>
<td>Mn(CO)₂⁺</td>
<td>14.81 ± 0.22</td>
<td>2</td>
</tr>
<tr>
<td>83</td>
<td>Mn(CO)⁺</td>
<td>15.98 ± 0.09</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>MeMn⁺</td>
<td>15.99 ± 0.18</td>
<td>2</td>
</tr>
<tr>
<td>55</td>
<td>Mn⁺</td>
<td>17.98 ± 0.02</td>
<td>2</td>
</tr>
</tbody>
</table>
for which \( D(Sn-Mn) = 9.30 - 6.93 = 2.37 \pm 0.30 \text{ eV} = 54.7 \pm 6.9 \text{ kcal/mole}. \)

Similarly, using equation [A-5], the tin-manganese ionic bond dissociation energy in \( \text{Me}_3\text{SnMn(CO)}_5^+ \) is given by

\[
D(\text{Me}_3\text{Sn-Mn(CO)}_5^+) = A(\text{Me}_3\text{Sn}^+) - I(\text{Me}_3\text{SnMn(CO)}_5) \quad \text{[III-11]}
\]

for which \( D(Sn-Mn^+) = 9.30 - 8.30 = 1.00 \pm 0.09 \text{ eV} = 23.1 \pm 2.1 \text{ kcal/mole}. \)

\( \text{Me}_3\text{PbMn(CO)}_5 \)

The overall appearance of the 50 eV, monoisotopic mass spectrum of \( \text{Me}_3\text{PbMn(CO)}_5 \), Table III-10, was very similar to its tin and germanium analogs. Again, under electron impact the ions \( \text{Me}_3\text{PbMn(CO)}_5^+ \) and \( \text{Me}_2\text{PbMn(CO)}_n^+ \;(n = 0-5) \) were produced, indicating that the major fragmentation pathway involved the initial loss of a methyl group followed by stepwise carbonyl losses. This breakdown scheme was supported by the observed metastable transitions as given in Table III-11. In addition, the mass spectrum of \( \text{Me}_3\text{PbMn(CO)}_5 \) exhibits the clearly resolved ions \( \text{MePbMn(CO)}_n^+ \;(n = 4,5) \) as well as small, unresolved ions \( \text{MePbMn(CO)}_n^+ \;(n = 1-3) \). Consequently, it may be assumed that a secondary fragmentation pathway also occurs, namely, the initial loss of two methyl groups followed by stepwise carbonyl losses.
TABLE III-10

Mass Spectrum for Me₃PbMn(CO)₅

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
<th>m/e</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>Me₃PbMn(CO)⁺⁷</td>
<td>6.16</td>
<td>349</td>
<td>Me₂PbMn(CO)⁺</td>
<td>6.38</td>
</tr>
<tr>
<td>433</td>
<td>Me₂PbMn(CO)⁺⁵</td>
<td>73.84</td>
<td>347</td>
<td>C₂H₄PbMn(CO)⁺</td>
<td>0.85</td>
</tr>
<tr>
<td>418</td>
<td>MePbMn(CO)⁺</td>
<td>0.81</td>
<td>336</td>
<td>{Me₂PbMn(CO)⁺ }</td>
<td>0.08</td>
</tr>
<tr>
<td>405</td>
<td>Me₂PbMn(CO)⁺⁴</td>
<td>7.25</td>
<td>335</td>
<td>{C₃H₆PbMn(CO)⁺ }</td>
<td>0.70</td>
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<tr>
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<td>C₂H₄PbMn(CO)⁺⁴</td>
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<tr>
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<td>333</td>
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</tr>
<tr>
<td>377</td>
<td>Me₂PbMn(CO)⁺³</td>
<td>4.16</td>
<td>321</td>
<td>Me₂PbMn(CO)⁺</td>
<td>5.94</td>
</tr>
<tr>
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<tr>
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<td>{C₃H₈PbMn⁺ }</td>
<td>0.81</td>
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<tr>
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<td>------</td>
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<tr>
<td>$m^+_1 \rightarrow m^+_2 + m_3$</td>
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<td>Assigned Transition</td>
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</tr>
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<td></td>
<td>Observed</td>
<td>Calculated</td>
<td></td>
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</tr>
<tr>
<td>448 → 433 + 15</td>
<td>418.54</td>
<td>418.50</td>
<td>$\text{Me}_3\text{PbMn(CO)}_5^+ \rightarrow \text{Me}_2\text{PbMn(CO)}_5^+ + \cdot \text{Me}$</td>
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</tr>
<tr>
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<td>378.81</td>
<td>$\text{Me}_2\text{PbMn(CO)}_5^+ \rightarrow \text{Me}_2\text{PbMn(CO)}_4^+ + \text{CO}$</td>
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<td></td>
</tr>
<tr>
<td>405 → 389 + 16</td>
<td>373.60</td>
<td>373.63</td>
<td>$\text{Me}_2\text{PbMn(CO)}_4^+ \rightarrow \text{CH}_2\text{PbMn(CO)}_4^+ + \text{CH}_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>405 → 377 + 28</td>
<td>350.91</td>
<td>350.94</td>
<td>$\text{Me}_2\text{PbMn(CO)}_4^+ \rightarrow \text{Me}_2\text{PbMn(CO)}_3^+ + \text{CO}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>377 → 349 + 28</td>
<td>323.17</td>
<td>323.08</td>
<td>$\text{Me}_2\text{PbMn(CO)}_3^+ \rightarrow \text{Me}_2\text{PbMn(CO)}_2^+ + \text{CO}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>405 → 349 + 56</td>
<td>300.81</td>
<td>300.74</td>
<td>$\text{Me}_2\text{PbMn(CO)}_4^+ \rightarrow \text{Me}_2\text{PbMn(CO)}_2^+ + \text{CO} + \text{CO}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>349 → 321 + 28</td>
<td>295.17</td>
<td>295.25</td>
<td>$\text{Me}_2\text{PbMn(CO)}_2^+ \rightarrow \text{Me}_2\text{PbMn(CO)}^+ + \text{CO}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>253 → 223 + 30</td>
<td>196.52</td>
<td>196.56</td>
<td>$\text{Me}_3\text{Pb}^+ \rightarrow \text{MePb}^+ + \text{C}_2\text{H}_6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308 → 223 + 85</td>
<td>161.53</td>
<td>161.46</td>
<td>$\text{Me}_3\text{PbMn}^+ \rightarrow \text{MePb}^+ + \text{Me}_2\text{Mn}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293 → 208 + 85</td>
<td>147.78</td>
<td>147.66</td>
<td>$\text{Me}_2\text{PbMn}^+ \rightarrow \text{Pb}^+ + \text{Me}_2\text{Mn}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>448 → 253 + 195</td>
<td>143.06</td>
<td>142.88</td>
<td>$\text{Me}_3\text{PbMn(CO)}_5^+ \rightarrow \text{Me}_3\text{Pb}^+ + \cdot \text{Mn(CO)}_5$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In common with both the germanium and tin analogs, many ions were observed due to hydrogen losses and/or rearrangements from the methyl groups attached to the lead atom, while no ions were found due to carbon-oxygen bond cleavage in the carbonyl groups attached to the manganese atom.

The rearrangement ion MeMn$^+$ was also observed in the mass spectrum of Me$_3$PbMn(CO)$_5$.

Ions containing only one metal atom corresponded to 59% of the total ion current when the ion source was cooled (18°C), and 83% when the ion source was not cooled (94°C). Hence, it may be assumed that extensive thermal pyrolysis of Me$_3$PbMn(CO)$_5$ was occurring at the higher temperature.

The appearance potentials for the major ions that were not overlapped with other ions are given in Table III-12. The low value of the appearance potential of Me$_3$Pb$^+$ and the observation of the metastable at m/e = 143.06 indicate that the ion Me$_3$Pb$^+$ was formed according to the process

$$\text{Me}_3\text{PbMn(CO)}_5 + e \rightarrow \text{Me}_3\text{Pb}^+ + \cdot\text{Mn(CO)}_5 + 2e \quad [\text{III-12}]$$

Therefore, in a manner similar to that used for the previous compounds in this series, the lead-manganese bond dissociation energy in Me$_3$PbMn(CO)$_5$ can be obtained from
TABLE III-12
Appearance Potentials for $\text{Me}_3\text{PbMn(CO)}_5$

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion</th>
<th>Appearance Potential (eV)</th>
<th>Determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>$\text{Me}_3\text{PbMn(CO)}_5^+$</td>
<td>7.86 ± 0.13</td>
<td>14</td>
</tr>
<tr>
<td>433</td>
<td>$\text{Me}_2\text{PbMn(CO)}_5^+$</td>
<td>8.34 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>405</td>
<td>$\text{Me}_2\text{PbMn(CO)}_4^+$</td>
<td>10.65 ± 0.06</td>
<td>2</td>
</tr>
<tr>
<td>390</td>
<td>$\text{MePbMn(CO)}_4^+$</td>
<td>11.38 ± 0.20</td>
<td>2</td>
</tr>
<tr>
<td>377</td>
<td>$\text{Me}_2\text{PbMn(CO)}_3^+$</td>
<td>11.42 ± 0.05</td>
<td>2</td>
</tr>
<tr>
<td>349</td>
<td>$\text{Me}_2\text{PbMn(CO)}_2^+$</td>
<td>11.87 ± 0.01</td>
<td>2</td>
</tr>
<tr>
<td>321</td>
<td>$\text{Me}_2\text{PbMn(CO)}^+$</td>
<td>11.93 ± 0.09</td>
<td>2</td>
</tr>
<tr>
<td>308</td>
<td>$\text{Me}_3\text{PbMn}^+$</td>
<td>11.84 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>293</td>
<td>$\text{Me}_2\text{PbMn}^+$</td>
<td>13.63 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>278</td>
<td>$\text{MePbMn}^+$</td>
<td>15.92 ± 0.05</td>
<td>2</td>
</tr>
<tr>
<td>263</td>
<td>$\text{PbMn}^+$</td>
<td>18.88 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>253</td>
<td>$\text{Me}_3\text{Pb}^+$</td>
<td>8.92 ± 0.07</td>
<td>22</td>
</tr>
<tr>
<td>238</td>
<td>$\text{Me}_2\text{Pb}^+$</td>
<td>12.15 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>223</td>
<td>$\text{MePb}^+$</td>
<td>12.53 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>208</td>
<td>$\text{Pb}^+$</td>
<td>15.10 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>111</td>
<td>$\text{Mn(CO)}_2^+$</td>
<td>14.13 ± 0.04</td>
<td>2</td>
</tr>
<tr>
<td>83</td>
<td>$\text{Mn(CO)}^+$</td>
<td>15.13 ± 0.19</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>$\text{MeMn}^+$</td>
<td>13.63 ± 0.09</td>
<td>2</td>
</tr>
<tr>
<td>55</td>
<td>$\text{Mn}^+$</td>
<td>18.94 ± 0.14</td>
<td>2</td>
</tr>
</tbody>
</table>
\[ D(\text{Me}_3\text{Pb-Mn(CO)}_5) = A(\text{Me}_3\text{Pb}^+) - I(\text{Me}_3\text{Pb}^-) \quad [\text{III-13}] \]

provided that the ionization potential of the trimethylplumbyl radical is known. To date however, no energetic measurements on this radical species have been made. Nevertheless, an estimate, \( I(\text{Me}_3\text{Pb}^-) = 6.89 \pm 0.44 \) eV, can be obtained from thermochemical and electron impact energetic considerations as described in Appendix G. Using this value and the observed appearance potential for \( \text{Me}_3\text{Pb}^+ \), the lead-manganese bond in \( \text{Me}_3\text{PbMn(CO)}_5 \) is

\[ D(\text{Pb-Mn}) = 8.92 - 6.89 = 2.03 \pm 0.51 \text{ eV} = 46.8 \pm 11.8 \text{ kcal/mole}. \]

Also, using equation [A-5], the lead-manganese ionic bond dissociation energy in \( \text{Me}_3\text{PbMn(CO)}_5^+ \) is given by

\[ D(\text{Me}_3\text{Pb-Mn(CO)}_5^+) = A(\text{Me}_3\text{Pb}^+) - I(\text{Me}_3\text{PbMn(CO)}_5) \quad [\text{III-14}] \]

for which \( D(\text{Pb-Mn}^+) = 8.92 - 7.86 = 1.06 \pm 0.20 \) eV = 24.4 ± 4.6 kcal/mole.

**Thermal Pyrolysis of \( \text{Me}_3\text{SnMn(CO)}_5 \)**

The thermal pyrolysis of trimethyltin manganese pentacarbonyl was carried out in the quartz molecular flow reactor. Appropriate ion intensities were monitored at reactor temperatures from 64°C to 579°C at which temperature the ion current for \( \text{Me}_3\text{SnMn(CO)}_5^+ \) was reduced to 1% of its
former value. As shown in Figure III-4 by the solid curve, a substantial increase in the ratio of the Me$_3$Sn$^+$/Me$_3$SnMn-(CO)$_5^+$ ion currents (at an ionizing energy of 50 eV) occurred over this temperature range.

In previous studies (41, 42), large ion current ratio increases of this type indicated that free radical species were being formed. If this were the case for Me$_3$SnMn(CO)$_5$, then as the reactor temperature increased, the appearance potential for the ion Me$_3$Sn$^+$ should decrease approaching the ionization potential of Me$_3$Sn. (123). However, the average of twelve appearance potential measurements for the ion Me$_3$Sn$^+$ at a reactor temperature of 675°C yielded a value of 9.49 ± 0.08 eV, which is higher than the appearance potential (9.30 ± 0.04 eV) for the same ion produced by electron bombardment of Me$_3$SnMn(CO)$_5$ at room temperature. Clearly then, at high temperatures the ion Me$_3$Sn$^+$ is being formed neither from the fragmentative ionization process [III-9], nor from the ionization of the trimethylstanyl radical species.

In order to ascertain how the ion Me$_3$Sn$^+$ was formed, a 50 eV mass spectrum was recorded over the mass range m/e = 55-360 for the species effusing from the reactor at a temperature of 590°C. The only ions observed in this
FIGURE III-4

THERMAL PYROLYSIS OF
Me₃SnMn(CO)₅
spectrum were \( \text{Me}_n\text{Sn}^+ \) (\( n = 0-4 \)). In addition, a rather intense metastable ion was observed for the process

\[
\text{Me}_3\text{Sn}^+ \rightarrow \text{Me}_2\text{Sn}^+ + \text{Me}^+ \quad \text{[III-15]}
\]

(\( m/e \) observed = 136.40, \( m/e \) calculated = 136.36). It should be pointed out that in the room temperature mass spectrum of \( \text{Me}_3\text{SnMn(CO)}_5 \): (i) the ion \( \text{Me}_4\text{Sn}^+ \) was not observed, and (ii) although the metastable at \( m/e = 136.40 \) may have been present, it was certainly far less intense than that found at the higher temperature.

Furthermore, as shown by the dashed curve in Figure III-4, the ratio of the \( \text{Me}_3\text{Sn}^+ / \text{Me}_2\text{Sn}^+ \) ion currents decreased from an initially high value to a much lower value as the reactor temperature was increased. The high, low temperature, ratio was similar to that observed for these same two ions formed in the room temperature mass spectrum of \( \text{Me}_3\text{SnMn(CO)}_5 \), while the low, high temperature, ratio was precisely the same as that found for these two ions in the mass spectrum of \( \text{Me}_4\text{Sn} \) (131).

Moreover, when tetramethylditin was introduced into the reactor at a temperature of 697°C, the average of eight determinations for the appearance potential of the ion \( \text{Me}_3\text{Sn}^+ \) was found to be 9.42 ± 0.05 eV. This was in excellent agreement with the observed appearance potential of the same
ion formed when $\text{Me}_3\text{SnMn(CO)}_5$ was introduced into the reactor.

All of these observations are consistent with the assumption that at high reactor temperatures $\text{Me}_3\text{SnMn(CO)}_5$ reacts in some way to form the molecular species $\text{Me}_4\text{Sn}$. The ion $\text{Me}_3\text{Sn}^+$ is subsequently produced according to the process

$$\text{Me}_4\text{Sn} + e^+ \rightarrow \text{Me}_3\text{Sn}^+ + \text{Me}^+ + 2e^- \quad [\text{III}-16]$$

A possible reaction scheme for the production of $\text{Me}_4\text{Sn}$ could involve the initial, thermally induced cleavage of the tin-manganese bond in $\text{Me}_3\text{SnMn(CO)}_5$ to produce $\text{Me}_3\text{Sn}^-$ and $\cdot\text{Mn(CO)}_5$ radicals. Since this particular reactor had a large ratio of internal surface to effusion orifice area (4000:1), then the residence time for the species inside the reactor would be rather long, and these species would experience many wall collisions before exiting through the effusion orifice. Consequently, at a reactor temperature of approximately 600°C, any $\cdot\text{Mn(CO)}_5$ radicals would probably decompose completely depositing a metallic film of manganese on the reactor walls, and liberating molecular carbon monoxide (11). This then would explain the absence of Mn containing ions in the high temperature mass spectrum.

The other radical species, $\text{Me}_3\text{Sn}^-$, could also decompose
to form methyl radicals and metallic tin. However, if the lifetime of the Me$_3$Sn species was sufficient to allow two such radicals to unite on the reactor walls, then the species Me$_6$Sn$_2$ would be formed. Hexamethyllditin could then disproportionate to form Me$_4$Sn. This type of disproportion has been previously observed for other alkyl distannanes (133).

In addition, it should be pointed out that when the analogous compound Me$_3$SnCo(CO)$_4$ was placed in a commercial mass spectrometer having an inlet temperature of 200-230°C, no Co containing ions were observed. This result was explained by the pyrolysis of Me$_3$SnCo(CO)$_4$ to give metallic cobalt, carbon monoxide, and hexamethyllditin (101).
CONCLUSIONS

Since all of the mass spectra and ion energetics for the series \( \text{Me}_3\text{M-Mn(CO)}_5 \) (\( \text{M} = \text{Si, Ge, Sn, Pb} \)) were recorded using the same instrument and under the same operating conditions, it should be possible to derive some general conclusions regarding the nature of the electron impact induced fragmentation. However, before attempting to compare the mass spectrometric results for this series of metal-metal bonded compounds, it should be emphasized that in any discussion of fragmentation by electron bombardment, the abundance of a particular ion in a mass spectrum is determined by the rate of formation and decomposition of that ion rather than its thermodynamic stability (138). For this reason, relative ion intensities cannot be used to support conclusions about bond fission processes in a molecule or its fragments. Nevertheless, valuable information about reaction pathways and bond energetics can be obtained from metastable transitions and electron impact energetic measurements.

As shown in Table III-13, the ionization potentials of the compounds of this study were low in value, similar to
<table>
<thead>
<tr>
<th>Species</th>
<th>I(eV)</th>
<th>Metal Atoms&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$SiMn(CO)$_5$</td>
<td>8.38 ± 0.15</td>
<td>8.15, 7.43</td>
</tr>
<tr>
<td>Me$_3$GeMn(CO)$_5$</td>
<td>8.34 ± 0.17</td>
<td>7.89, 7.43</td>
</tr>
<tr>
<td>Me$_3$SnMn(CO)$_5$</td>
<td>8.30 ± 0.05</td>
<td>7.34, 7.43</td>
</tr>
<tr>
<td>Me$_3$PbMn(CO)$_5$</td>
<td>7.86 ± 0.13</td>
<td>7.42, 7.43</td>
</tr>
<tr>
<td>CO</td>
<td>14.013 ± 0.004&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>*Me</td>
<td>9.840 ± 0.002&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Reference 136

<sup>b</sup> Reference 137
the ionization potentials of the metals involved rather than the substituent groups. Consequently, the electron withdrawn upon ionization can be considered to have been localized on one of the metal atoms, and for reasons cited below, specifically the Group IVB metal atom.

The mass spectra and metastable transitions observed for this series of compounds indicated that there were three fragmentation pathways with the molecular ion as origin

\[
\begin{align*}
\text{Me}_3\text{MMn(CO)}_5^+ & \xrightarrow{a} \text{Me}_3\text{MMn(CO)}_4^+ + \text{CO} \\
\text{Me}_3\text{MMn(CO)}_5^+ & \xrightarrow{b} \text{Me}_2\text{MMn(CO)}_5^+ + \cdot\text{Me} \\
\text{Me}_3\text{MMn(CO)}_5^+ & \xrightarrow{c} \text{Me}_3\text{M}^+ + \cdot\text{Mn(CO)}_5 \\
\end{align*}
\]

The preferred pathway will depend on the relative energies required to break a Mn-CO, a M-Me, or a M-Mn bond in the molecular ion. Appearance potentials may be used to determine the approximate bond dissociation energy of different bonds in the molecular ion as indicated by equation [A-5], and for this series of compounds these energies are summarized in Table III-14.

Ions indicative of the elimination of carbon monoxide (pathway a) may have been present in the mass spectra of the germanium, tin and lead compounds, but they were very low in
### TABLE III-14

**Ionic Bond Dissociation Energies in the Molecular Ion**

Me$_3$MMn(CO)$_5$ (M = Si, Ge, Sn, Pb)

<table>
<thead>
<tr>
<th>Molecular Ion Bond Dissociation Energies (eV)</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(Mn-CO$^+$)</td>
<td>1.18 ± 0.20</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>D(M-Me$^+$)</td>
<td>2.52 ± 0.19</td>
<td>2.75 ± 0.25</td>
<td>1.02 ± 0.08</td>
<td>0.48 ± 0.15</td>
</tr>
<tr>
<td>D(M-Mn$^+$)</td>
<td>1.40 ± 0.26</td>
<td>1.42 ± 0.33</td>
<td>1.00 ± 0.09</td>
<td>1.06 ± 0.20</td>
</tr>
</tbody>
</table>
abundance and extensively overlapped with other species which precluded any appearance potential measurements. In contrast, ions of the type $\text{Me}_3\text{SiMn(CO)}_n^+$ ($n = 0-5$) were quite abundant in the mass spectrum of $\text{Me}_3\text{SiMn(CO)}_5$, and from the molecular ion bond dissociation energies, the elimination of a carbonyl group is the preferred fragmentation route in this compound.

Excluding pathway a, the molecular ion bond dissociation energies indicate that as the atomic weight of M increases, the favoured fragmentation route changes from cleavage of the metal-metal bond (pathway c) to the cleavage of the Group IVB metal-methyl bond (pathway b). This result is not unexpected since it is well known (see Appendix G) that Group IVB metal-carbon bond dissociation energies decrease in the series $(\text{Si-C}) > (\text{Ge-C}) > (\text{Sn-C}) > (\text{Pb-C})$.

It should be pointed out that in both pathways b and c, ions are produced in which the Group IVB metal is bonded to three other groups, in common with the mass spectra of many Group IVB compounds (70, 124, 131, 135). This tervalent tendency would suggest that the result of primary ionization was the loss of one of the bonding electrons between the Group IVB metal and either a methyl group or the manganese pentacarbonyl moiety (70, 131).
The molecular and ionic metal-metal bond dissociation energies calculated for each compound in this series are summarized in Table III-15. Within the quoted errors, and in common with other studies (10, 105, 140, 141, 142), the trend observed in the ionic bond dissociation energies holds for the neutral bond energies as well. The ionic values, however, are numerically much smaller than the neutral values which supports the assumption that the electron removed upon ionization was a bonding electron between the two metals.

It should be pointed out that the values listed in Table III-15 were calculated with the implicit assumption of no excess kinetic or excitation energy being associated with the electron impact process. For this reason, bond dissociation energies obtained from appearance potential measurements may be somewhat higher than their true values. However, all of the ion energetics measured in this study were obtained with the ion source at a temperature of approximately 20°C. Hence, the amount of excess kinetic and excitation energy imparted to molecules before ionization by collisions with the walls of the ionization chamber should be very small.

Furthermore, according to Stevenson's rule (139), when a molecule is ionized and then dissociates, the positive charge will usually reside on that fragment having the
**TABLE III-15**

Metal-Metal Bond Dissociation Energies

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Dissociation Energies (kcal/mole)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D(M-Mn)</td>
<td>D(M-Mn$^+$)</td>
</tr>
<tr>
<td>Me$_3$Si-Mn(CO)$_5$</td>
<td>57.0 ± 6.7</td>
<td>32.2 ± 6.0</td>
</tr>
<tr>
<td>Me$_3$Ge-Mn(CO)$_5$</td>
<td>62.5 ± 7.8</td>
<td>32.7 ± 7.6</td>
</tr>
<tr>
<td>Me$_3$Sn-Mn(CO)$_5$</td>
<td>54.7 ± 6.9</td>
<td>23.1 ± 2.1</td>
</tr>
<tr>
<td>Me$_3$Pb-Mn(CO)$_5$</td>
<td>46.8 ± 11.8</td>
<td>24.4 ± 4.6</td>
</tr>
</tbody>
</table>
lowest ionization potential, since this gives the most stable arrangement of products, i.e., the products have near zero kinetic energy. For the compounds in this study, the ionization potentials, \( I(\text{Me}_3\text{M}^+) \), \((\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb})\) \( (123) \) were, in every case, lower than that of the manganese penta-carbonyl radical, \( I(\cdot\text{Mn(CO)}_5) = 8.44 \pm 0.10 \text{ eV } (39) \). Therefore, it may be assumed that the fragments produced in the dissociation process

\[
\text{Me}_3\text{MMn(CO)}_5 + e \rightarrow \text{Me}_3\text{M}^+ + \cdot\text{Mn(CO)}_5 + 2e \quad [\text{III-18}]
\]

\((\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb})\) had little or no kinetic energy. In any case, kinetic and excitation energy corrections to the appearance potentials measured for process \([\text{III-18}]\) would be very small compared to the magnitude of the energy involved, and hence these two excess energy terms appear to be justifiably neglected.

Theoretically, the errors quoted in Table III-15 prohibit any firm conclusions to be obtained concerning the effect of changing the Group IVB metal on the metal-metal bond dissociation energy in the series \( \text{Me}_3\text{M-Mn(CO)}_5 \) \((\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb})\), and this is graphically illustrated in Figure III-5(a). Nevertheless, it is interesting to note that the trend indicated in this work is \( D(\text{Ge-Mn}) > D(\text{Si-Mn}) \)
FIGURE III-5

BOND DISSOCIATION ENERGIES
AND ELECTRONEGATIVITIES
> D(Sn-Mn) > D(Pb-Mn). Also worthwhile noting is this same irregular trend in the electronegativities of the sp³ hybridized Group IVB elements as shown in Figure III-5(b), which have been attributed to the filling of inner shells which affects the screening of the valence electrons (143).

The electronegativity of manganese has been measured as 1.60 (144), and consequently the largest difference between the electronegativities of the two metals in the series Me₃MMn(CO)₅ (M = Si, Ge, Sn, Pb) occurs for the germanium compound. Then, according to Pauling (145), the Ge-Mn bond has the highest ionic character, and therefore should have the greatest bond strength.

Although it is unwise to correlate bond dissociation energies with chemical reactivity information, it should be mentioned that reactions which occur easily with Me₃SnMn(CO)₅ often proceed with difficulty (or not at all) with Me₃GeMn-(CO)₅ (146).

It seems clear that the cooled ion source arrangement used in this work was very useful for obtaining reliable mass spectrometric information for temperature sensitive compounds, especially Me₃PbMn(CO)₅. Consequently, the techniques developed in this work could be extended to other volatile transition metal derivatives of Group IVB, notably the series
Me₃M-Co(CO)₄ (M = Si, Ge, Sn, Pb) which are known to decompose in commercial instruments (101).

However, obtaining metal-metal bond dissociation energies by electron impact methods is hindered by the fact that very few organometallic radical ionization potentials are known. To date, the production of such radicals has relied on thermal decomposition methods. However, as illustrated by the thermal decomposition of Me₃SnMn(CO)₅ in this work, the main problem is finding suitable compounds which will thermally generate the desired radical species.

A more promising method of obtaining organometallic radicals appears to be the mass spectrometric technique in which two electron beams are used -- an intense pulsed beam to form neutral fragments, including free radicals, and a second continuous beam to ionize them (147, 148, 149, 150, 151). Indeed, using this method coupled with a monoenergetic source of electrons (152) as the second beam would appear to be a very powerful technique for obtaining accurate radical ionization potentials as well as much more precise appearance potentials. Such a system would then allow bond energy calculations to be obtained which would have much lower uncertainties than are presently possible to achieve.
REFERENCES


31. Vacuum Accessories Corp. of America, Huntington Station, N.Y., MV-25-XL Precision Gas Metering Valve Specifications.

32. S. Dushman, ibid. page 82.


Appendix A. Fundamentals and Terminology of Mass Spectrometry

Electron Impact Energetics

The kinetic energy, \( T \), acquired by an electron (initially at rest) moving through an accelerating potential of \( V \) volts is

\[
T = \frac{1}{2} mv^2 = eV
\]  \hspace{1cm} \text{[A-1]}

where \( m \) is the mass of the electron

\( v \) is the velocity of the electron

and \( e \) is the charge of the electron.

An electron with 50 electron volts energy travels with a velocity of about \( 1.8 \times 10^9 \) cm/sec. If this electron "collides" with a neutral molecule having an average molecular diameter of \( 10\, \text{Å} \), then the time required for this electron to "travel through" the molecule is about \( 5.7 \times 10^{-17} \) seconds. Molecular vibrational periods are of the order of \( 10^{-14} \) seconds. Consequently, the impacting electron ionizes the molecule in a fraction of the vibrational period. This rather simplistic description of the ionization process involves an electronic reorganization in a time that is sufficiently short to leave the nuclear configuration
relatively unchanged. This is the essence of the Franck-Condon principle.

Some of the consequences involved in the ionization of a molecule are illustrated by the representative potential energy curves for a diatomic molecule XY as shown in Figure A-1. The vertical dashed lines represent the limits of the Franck-Condon region. Transitions from the ground state (curve 1) to an ionic state (curve 2) will give rise to molecular ions $XY^+$ that are vibrationally excited, and also to fragment ions $X^+$. The products resulting from a dissociative ionization may possess a kinetic energy ranging from zero up to $E_k$.

For polyatomic molecules it becomes impractical to interpret electron impact processes in terms of potential surfaces. A statistical approach to explain the mass spectra of polyatomics has been developed (14). The basic hypothesis is that upon "vertical" ionization the molecular ion formed does not dissociate within the time of one vibration. The excess energy is not retained at the bond from which the electron was removed in ionization, but is rapidly and randomly distributed over all the internal degrees of freedom. Fragmentation occurs when sufficient vibrational energy (equal to the dissociation energy) is concentrated in a
Figure A-1

Potential energy curves involved in the dissociative ionization of a diatomic molecule by electron impact.
particular bond.

An appearance potential is defined as the minimum energy required to produce a given ion and its accompanying neutral fragments (if any) from a given molecule, ion, or radical. Associated with an appearance potential, then, is both ionization and dissociation. For a diatomic molecule, the appearance potential of $X^+$ from $XY$ is shown in Figure A-1 as $A(X^+)$. Since products may be in excited states and may possess a certain amount of kinetic energy, experimentally determined appearance potentials may be somewhat greater than values corresponding to theoretical definitions. An appearance potential for a polyatomic molecule can be considered to be the energy required to produce a parent ion with enough excitation energy necessary to produce the fragment of interest, with sources of error being the excess energy required in the parent ion to produce this decay, as well as those already cited for diatomics.

A special case of the appearance potential is the ionization potential which is defined as the amount of energy required to remove to infinite distance the least strongly bound electron from an atomic or molecular orbital of the neutral particle to form the corresponding atomic or molecular ion. For a diatomic (Figure A-1), this value is $I_0(XY)$, and
would correspond to an adiabatic transition from curve 1 to curve 2. The experimentally observed ionization potential is \( I(XY) \), and hence electron impact values of ionization potentials are usually considered to constitute upper limits to the true adiabatic value.

If one neglects excitation and kinetic energies, then an appearance potential is simply the heat of the reaction by which an ion is formed. For the reaction

\[
XY + e \rightarrow X^+ + Y^* + 2e
\]  

[A-2]

and using the usual relations of thermochemistry, one can obtain the relation

\[
A(X^+) = \Delta H_{\text{rxn}} = \Delta H_f(X^+) + \Delta H_f(Y^*) - \Delta H_f(XY)
\]  

[A-3]

If the heats of formation for the last two terms of this equation are known, then one may calculate the heat of formation of gaseous positive ions.

Bond dissociation energies may also be calculated from the relations

\[
D(X-Y) = A(X^+) - I(X^*)
\]  

[A-4]

and

\[
D(X-Y^+) = A(X^+) - I(XY)
\]  

[A-5]

It must be noted that bond dissociation energies calculated in this manner are subject to a certain amount of error because of the neglect of excitation and kinetic energies.
associated with values determined from electron impact measurements.

Ionization and appearance potentials are determined experimentally from plots of the intensity of the ion under study as a function of electron energy. Such a plot is known as an ionization efficiency curve. For instruments employing nonmonoenergetic electron beams, the general appearance (Figure A-2) of this curve consists of four sections: (i) a curved portion for the first volt or so above the ionization threshold, (ii) an almost linear portion for the next 10 to 20 volts, (iii) a rather broad maximum between 50 and 100 volts, and (iv) a gradual decrease for higher voltages.

The exact form of the curve depends to a considerable extent upon the nature of the ion. For ions formed from a simple ionization, the extent of the initial curvature is smaller and the slope of the linear portion is greater than is the case for fragment ions formed by complicated ionization mechanisms.

Ideally, the value of the appearance potential for an ion should be that point on the energy scale at which a signal for the ion first appears. In actual practice however, factors such as signal-to-noise ratio of the
FIGURE A-2

GENERAL SHAPE OF AN IONIZATION EFFICIENCY CURVE
detection system, the lack of a monoenergetic electron beam, space charge effects, contact potentials, and interfering external fields prohibit a direct measurement of appearance potentials. Several empirical techniques have been developed (15, 16, 17) to extract the desired information from ionization efficiency curves. They are all based on a common idea: comparison of the unknown data with that for a calibrant whose ionization potential is well known.

The method used in this study was the extrapolated voltage difference method of Warren (17). The experimental procedure has been described previously (11). A brief description of the method as well as the computer program written to analyze the data is given in Appendix C.

Positive Ion Mass Spectra

The term mass spectrum is generally defined as the relative proportion of positive ions observed in the ionization and dissociation of neutral molecules by electron bombardment. Parent ions (formed by the removal of a single electron from the neutral molecule) and fragment ions (formed by various bond cleavages from the parent-molecule ion) usually constitute the array of peaks in a complete spectrum.
The mass spectra of some compounds exhibit rather intense ions whose origin cannot be described by the assumption of simple bond cleavages in the parent-molecule ion. These ions are termed "rearrangement" ions, and they are formed as a result of an intramolecular reorganization accompanying the fragmentation process. An excellent comprehensive review on the classification, energetics, and kinetics of rearrangement processes has recently been published (20).

Since the majority of elements have stable, naturally occurring isotopes, and since a mass spectrometer separates ions according to their masses, isotope peaks appear in most spectra. The pattern to be expected from a particular combination of polyisotopic elements can be predicted, and a computer program written to accomplish this is described in Appendix D.

Under low resolution conditions it is not uncommon to find that some of the isotopes for different ions have the same nominal m/e values. The effect of this overlap is to add the intensities at the common m/e values. The obvious solution to this overlap problem is high resolution, but with the mass spectrometer used for this study high resolution is impractical. The other choice is to deconvolute
the overlapped low resolution spectra by using a heuristic approach coupled with a computer program. Details, as well as an illustrative example of this technique may be found in Appendix D.

Once the overlapped portions of a spectrum have been deconvoluted within the limits of experimental error, and all of the isotopic contributions have been reduced to mono-isotopic form, the most intense ion is designated as the "base peak" and assigned a value of 100. Abundance values for all other ions in the spectrum are expressed as percentages of the base peak.

In a mass spectrometer it is possible for an ion that has been accelerated from the ionization chamber to fragment during its flight towards the magnetic analyzer. The relationships governing the observation and identification of these in-flight fragmentations were first described by Hipple and Condon (18). The fragmentation process is known as a metastable transition

\[ m_1^+ \rightarrow m_2^+ + m_3 \]  \hspace{1cm} [A-7]

which involves a "parent" ion of mass \( m_1 \) decomposing to a "daughter" fragment ion of mass \( m_2 \), and a neutral particle of mass \( m_3 \) (normally a stable molecule or radical). These broad, diffuse metastable peaks have relative abundances of
about 0.5% (or lower) of the base peak, and appear at an apparent mass, \( m^* \), given by

\[
    m^* = \frac{m_2^2}{m_1}
\]

[A-8]

The appearance of a metastable ion gives almost certain evidence that a one-step decomposition process has taken place, and therefore yields very useful information concerning the fragmentation process. In practice, the assignment of metastable transitions is by no means routine, due to the many combinations of \( m_1 \) and \( m_2 \) which can yield approximately the same \( m^* \). A computer program has been written to facilitate this analysis and it is described in Appendix E.
Appendix B. The Relationship Between Observed Ion Intensities and the Partial Pressures of Molecular Species in an Effusion Reactor

Consider an isothermal vessel containing a gas at some low pressure $p_1$. Suppose one wall of this vessel is infinitely thin and contains a small orifice through which the gas can effuse into an adjacent region, where the pressure is $p_2$ ($p_1 > p_2$) at the same temperature. The linear dimensions of the small orifice are such that they are much smaller than the mean free path of the gas molecules at either pressure. Under such conditions, the rate of flow is limited, not by collisions between molecules, but by collisions of molecules with the walls. Under such conditions flow is designated as molecular flow.

The number of molecules of a gas that strike unit area per unit time is given by the relation (19)

$$\nu = \frac{1}{4} nu$$  \[[B-1]\]

where $n$ is the number of molecules per unit volume

and $u$ is the average molecular velocity.

If $m$ is the mass of a molecule, then $nm$ is simply the
density of the gas $\rho$. From the ideal gas law density is given by
\[
\rho = \frac{M_p}{RT} = \text{nm} \quad \text{[B-2]}
\]
where $M$ is the molecular weight
$R$ is the gas constant
and $T$ is the absolute temperature.

Substituting equation [B-2] into [B-1] yields
\[
\nu = \frac{up}{4kT} \quad \text{[B-3]}
\]
where $k$ is Boltzmann's constant.

Since the orifice is small compared to the mean free path, all molecules striking from either side will get through, and therefore a net transfer will take place
\[
\nu(1 \rightarrow 2) - \nu(2 \rightarrow 1) = \frac{u(p_1 - p_2)}{4kT} \quad \text{[B-4]}
\]
For the case where $p_2 \ll p_1$, $(p_1 - p_2) \approx p_1$, hence
\[
\nu(1 \rightarrow 2) = \frac{up_1}{4kT} \quad \text{[B-5]}
\]

The flow conditions in a mass spectrometer approach this case since the reactor pressure, $p_1$, is approximately $10^{-4}$ torr, the ion chamber pressure, $p_2$, is approximately $10^{-7}$ torr, and therefore $\nu(1 \rightarrow 2) \gg \nu(2 \rightarrow 1)$. For the effusion of a mixture of ideal gases we have for the i-th species
\[ \nu_i (1 \rightarrow 2) = \frac{p_i u_i}{4kT} \]  

[B-6]

The molecules of the \( i \)-th species traverse the ionization region where a fraction of them are ionized, transmitted through the mass analyzer, and detected as an ion current \( I_{i+} \) which is given by the relation (1)

\[ I_{i+} = n_i \varphi \sigma_i S_{i+} \tau \]  

[B-7]

where \( n_i \) is the number of molecules in the ionization region

\( \varphi \) is the ionizing electron flux

\( \sigma_i \) is the partial ionization cross section

\( S_{i+} \) is the electron multiplier detection efficiency for the ionic species \( i^+ \)

and \( \tau \) is the transmission coefficient of the mass spectrometer

For a beam of molecules moving through the ionization region

\[ n_i = \frac{\nu_i}{u_i} = \frac{c \nu_i (1 \rightarrow 2)}{u_i} \]  

[B-8]

where \( \nu_i \) is the number of molecules passing through the ionization region per second

and \( c \) is a constant dependent on the relative
position of the effusion orifice to ion chamber

Combination of equations [B-6], [B-7], and [B-8] gives

\[ I_{i+} = \frac{c \varphi \sigma_i \tau p_i S_{i+}}{4kT} \]  \[ \text{[B-9]} \]

Under a given set of operating conditions \( \varphi, S_{i+}, \) and \( \tau \) are constant. If it is assumed that \( \sigma_i \) is constant over a particular temperature range used in an effusion study, then equation [B-9] becomes

\[ P_i = c_i I_{i+T} \]  \[ \text{[B-10]} \]
Appendix C. FORTRAN IV Program for Interpretation of
Ionization Efficiency Curves

Ionization and appearance potentials are determined experimentally from plots of the intensity of the ion under investigation as a function of the ionizing electron energy. Such graphical representations are known as ionization efficiency curves, and the value for the ionization (or appearance) potential is that point on the electron energy scale at which a signal for the ion first appears. In practice, the energy of the ionizing electrons is not that indicated by monitoring devices because of contact potentials and other effects in the ion source of the mass spectrometer (153). Hence, in order to calibrate the electron energy scale, one measures the difference between the onset potential of the ion of interest and an ion of known ionization potential, usually one of the inert gases. Furthermore, in most mass spectrometers the bombarding electron beam is produced by thermionic emission from a heated metal filament and consequently the electrons have an energy distribution which is essentially Maxwellian in character (154). The effect of this electron energy spread
is to cause ionization efficiency curves to approach the energy axis in an asymptotic manner. Therefore, a major difficulty in the determination of appearance potentials from ionization efficiency curves is the interpretation of the curvature near threshold and the definition of the point of onset.

Although various methods (15, 16, 155) have been devised to overcome this difficulty, the one used exclusively in this work was the extrapolated voltage difference method of Warren (17). A calibrating gas (xenon) and the gaseous sample under investigation were simultaneously admitted to the ion source of the mass spectrometer and the partial pressures of each were made equal at an ionizing energy of 50 eV. The ionization efficiency curves (ion currents of 1% to 0.1% of the 50 eV value) for a particular ion from the sample and the calibrant gas were determined as illustrated in Figure C-1(a). The ratio of the slopes of the linear portions of these curves was determined, and the individual ion intensities, \( i^+ \), of either the sample ion or the calibrant ion curve were multiplied by this ratio to cause the linear portions to be parallel as shown in Figure C-1(b). Next, the voltage differences, \( \Delta V \), at various values of \( i^+ \) were determined from the curves. Finally a new plot of \( \Delta V \)
FIGURE C-1

APPEARANCE POTENTIAL DETERMINATION BY WARREN'S METHOD
versus $i^+$ was prepared, Figure C-1(c), and the resulting curve was linearly extrapolated to $i^+ = 0$. This intercept value was algebraically added to the ionization potential of the calibrant to obtain the appearance potential of the sample ion.

From the above description, it should be obvious that when carried out manually, this is a very tedious procedure, especially for large numbers of ionization efficiency curves. Consequently, in order to reduce the time required, and to eliminate personal bias in drawing the various curves, the raw ionization efficiency data was processed using a program written for a DEC PDP-10 computer. In this program, both the parallel adjustment and extrapolation procedures were carried out using standard linear least squares techniques, and the voltage differences were obtained with a cubic spline interpolation procedure (156). Periodically, appearance potentials were obtained manually and compared with those evaluated from the program, and in every case the results were in excellent agreement.
COMMON /PTS/XA(100),YA(100),XB(100),YB(100),YBS(100),
1LYBP(100)
COMMON /NPTS/NA,NB
COMMON /ALPHA/TITLE(15),LYNE(15)
CALL IFILE(1,'DATA')
101 LOOP=-1
100 CALL DPREP(RATIO,LOOP,NEW)
   LOOP=1
   TYPE 1
   1 FORMAT(1H1)
   CALL DAYTIME
   TYPE 3
   3 FORMAT(1H0,5X,'APPEARANCE (IONIZATION) POTENTIAL DETER
   1MINATION')
   TYPE 4,TITLE
   4 FORMAT(1H0,5X,'ION:'2X,15A5)
   TYPE 5,LYNE
   5 FORMAT(1H0,5X,'CONDITIONS:'2X,15A5)
   TYPE 6,RATIO
   6 FORMAT(1H0,5X,'LINEAR PORTION PARALLELISM INDICATOR ='
   1F9.5)
   TYPE 7
   7 FORMAT(1H0,20X,'XENON '+'32X,'UNKNOWN+'
   TYPE 71
   71 FORMAT(1H0,49X,'ORIGINAL'3X,'SMOOTHED'3X,'PARALLEL')
   TYPE 8
   8 FORMAT(16X,'E.A.V.'2X,'INTENSITY'8X,'E.A.V.'2X,3('INT
   1ENSITY'2X)/)
   J=MINO(NA,NB)
   DO 9 I=1,J
   TYPE 10,XA(I),YA(I),XB(I),YB(I),YBS(I),YBP(I)
   10 FORMAT(16X,F6.2,3X,F7.2,9X,F6.2,3X,3(F7.2,4X))
   9 CONTINUE
   IF(NA.EQ.NB)GO TO 11
   IF(NA.LT.NB)GO TO 12
   K=NA-J
   DO 13 I=1,K
   TYPE 14,XA(L),YA(L)
   14 FORMAT(16X,F6.2,3X,F7.2)
   13 CONTINUE
   GO TO 11
   12 K=NB-J
   DO 15 I=1,K
   TYPE 16,XB(L),YB(L),YBS(L),YBP(L)
   16 FORMAT(41X,F6.2,3X,3(F7.2,4X))
CONTINUE

TYPE 72

FORMAT(1H0,5X,'EXTRAPOLATED VOLTAGE DIFFERENCE RESULTS:')
CALL OMIT
CALL DIFF(S,DS,B,DB,R)
TYPE 17

FORMAT(1H0,10X,'LINE',11X,'SLOPE',6X,'CORRELATION',2X,'APPEARANCE POTENTIAL',3X,'DEVIATION')
TYPE 18

FORMAT(11X,'SLOPE',8X,'DEVIATION',4X,'COEFFICIENT',5X,'(EV)
1.5X,'(KCAL)',8X,'(EV)')
BK=B*23.0609
TYPE 19,S,DS,R,B,BK,DB

FORMAT(1H0,6X,E13.6,2X,E13.6,3X,F9.5,4X,F8.4,2X,F9.4,3X,1F10.6)
IF(NEW.EQ.1)GO TO 101
GO TO 100
STOP
END

SUBROUTINE DPREP(RATIO,LOO,NEW)
COMMON /PTS/XA(100),YA(100),XB(100),YB(100),YBS(100),YBP(100)
COMMON /NPTS/NA,NB
COMMON /ALPHA/TITLE(15),LYNE(15)
DIMENSION EAV(100),CURNT(100)
READ (1,30) TITLE

FORMAT(15A5)
IF (L00) 60,60,61

READ (1,30) LYN

VPI=4.0/15.0
FPR=0.5
LOOP=1

READ (1,31) BASE,N,IUP,START

FORMAT(F,2I,F)
IF (IUP.EQ.0)GO TO 32
EAV(1)=START
READ (1,34) (CURNT(I),I=1,N)

FORMAT(15F)
DO 33 I=1,N
CURNT(I)=CURNT(I)-BASE

30 FORMAT(15A5)
IF (L00) 60,60,61

60 READ (1,30) LYN

61 VPI=4.0/15.0
FPR=0.5
LOOP=1

42 READ (1,31) BASE,N,IUP,START

31 FORMAT(F,2I,F)
IF (IUP.EQ.0)GO TO 32
EAV(1)=START
READ (1,34) (CURNT(I),I=1,N)

34 FORMAT(15F)
DO 33 I=1,N
CURNT(I)=CURNT(I)-BASE

32 FORMAT(20H5)
33 CONTINUE
34 FORMAT(15F)
CONTINUE
DO 35 I=2,N
EAV(I)=EAV(I-1)+VPI*FPR
35 CONTINUE
GO TO 36
EAV(N)=START
READ(1,34)(CURNT(I),I=N,1,-1)
DO 37 I=1,N
CURNT(I)=CURNT(I)-BASE
37 CONTINUE
DO 38 I=N-1,1,-1
EAV(I)=EAV(I+1)-VPI*FPR
38 CONTINUE
IF(LOOP.NE.1)GO TO 39
NA=N
DO 40 I=1,NA
XA(I)=EAV(I)
YA(I)=CURNT(I)
40 CONTINUE
LOOP=2
READ(1,41)IAUTO
41 FORMAT(I)
IF(IAUTO.EQ.1)GO TO 42
READ(1,43)BASE,N
43 FORMAT(F,I)
READ(1,45)(EAV(I),CURNT(I),I=1,N)
45 FORMAT(10F)
DO 44 I=1,N
CURNT(I)=CURNT(I)-BASE
44 CONTINUE
NB=N
DO 46 I=1,NB
XB(I)=EAV(I)
YB(I)=CURNT(I)
46 CONTINUE
IF(IAUTO.EQ.0)GO TO 47
DO 48 I=1,NB
YBS(I)=YB(I)
48 CONTINUE
GO TO 49
47 YBS(1)=YB(1)
YBS(2)=YB(2)
YBS(NB-1)=YB(NB-1)
YBS(NB)=YB(NB)
L=NB-4
DO 50 I=1,L 
    YBS(I+2)=(-3.0*YB(I)+12.0*YB(I+1)+17.0*YB(I+2)+12.0*YB(I+3)-3.0*YB(I+4))/35.0 
50 CONTINUE
49 CALL SELECT(SA,SB) 
    RATIO=SA/SB 
    TEST=YBS(1)*RATIO 
    IF(TEST<5.0)51,51,52 
51 DO 53 I=1,NB 
    YBP(I)=YBS(I)*RATIO 
53 CONTINUE 
    GO TO 54 
52 DO 55 I=1,NB 
    YBP(I)=YBS(I) 
55 CONTINUE 
54 READ(1,41)NEW 
    RETURN 
END

SUBROUTINE SELECT(SA,SB) 
COMMON /PTS/XA(100),YA(100),XB(100),YB(100),YBS(100),YBP(100) 
COMMON /NPTS/NA,NB 
DIMENSION XAT(5),YAT(5),XBT(5),YBT(5),X(15),Y(15) 
    XAT(1)=XA(NA) 
    YAT(1)=YA(NA) 
    DO 10 I=1,4 
    XAT(I+1)=XA(NA-I) 
    YAT(I+1)=YA(NA-I) 
10 CONTINUE 
    L=0 
    DO 11 I=1,5 
    DO 12 J=5,I,-1 
    L=L+1 
    X(L)=XAT(I) 
    Y(L)=YAT(I) 
12 CONTINUE 
11 CONTINUE 
    CALL STLINE(X,Y,15,SA,DS,B1,DL,B2,DR,R,RP) 
    XBT(1)=XB(NB) 
    YBT(1)=YBS(NB)
DO 13 I=1,4
XBT(I+1)=XB(NB-I)
XBT(I+1)=YBS(NB-I)
13 CONTINUE
L=0
DO 14 I=1,5
DO 15 J=5,I,-1
L=L+1
X(L)=XBT(I)
Y(L)=YBT(I)
15 CONTINUE
14 CONTINUE
CALL STLINE(X,Y,15,SB,DS,B1,DB1,B2,DB2,R,RP)
RETURN
END

SUBROUTINE STLINE(X,Y,N,S,DS,B1,DB1,B2,DB2,R,RP)
DIMENSION X(N),Y(N)
DOUBLE PRECISION XI,YI,SUMX,SUMY,SUMXX,SUMYY,SUMXY,TOTA
1L,DENOX,DENOX,DENXY,DPS,DPDS,DPB1,DPDB1,DPB2,DPDB2,DPR,
2DPRP,CONST,D2
SUMX=0.0D0
SUMY=0.0D0
SUMXX=0.0D0
SUMYY=0.0D0
SUMXY=0.0D0
DO 10 I=1,N
XI=DBLE(X(I))
YI=DBLE(Y(I))
SUMX=SUMX+XI
SUMY=SUMY+YI
SUMXX=SUMXX+XI*XI
SUMYY=SUMYY+YI*YI
SUMXY=SUMXY+XI*YI
10 CONTINUE
TOTAL=DBLE(FLOAT(N))
DENOX=TOTAL*SUMXX-SUMX*SUMX
DENOX=TOTAL*SUMYY-SUMY*SUMY
DENXY=TOTAL*SUMXY-SUMX*SUMY
DPS=DENXY/DENOX
DPB1=(SUMY-DPS*SUMX)/TOTAL
DPR=DPS*DSQRT(DENOX/DENOY)
DPRP=-SUMX/DSQRT(TOTAL*SUMXX)
DPB2=-DPB1/DPS
CONST=DPS*DPS*(1.0DO/(DPR*DPRP)-1.0DO)/(TOTAL-2.0DO)
DPDB1=DSQRT(CONST*SUMXX/TOTAL)
DPDS=DSQRT(CONST)
D2=DPS*DPS
DPDB2=DSQRT(DPDB1*DPDB1/D2+DPB1*DPB1*DPDS*DPDS/(D2*D2)-12.0DO*DPRP*DPDB1*DPDS*DPB1/(D2*DPS))
S=SNGL(DPS)
DS=SNGL(DPDS)
B1=SNGL(DPB1)
DB1=SNGL(DPDB1)
B2=SNGL(DPB2)
DB2=SNGL(DPDB2)
R=SNGL(DPR)
RP=SNGL(DPRP)
RETURN
END

SUBROUTINE DIFF(S,DS,B,DB,R)
COMMON /PTS/XA(100),YA(100),XB(100),YB(100),YBS(100),1YBP(100)
COMMON /NPTS/NA,NB
DIMENSION CA(4,100),CB(4,100),X(500),Y(500)
DIMENSION XAX(100),YAY(100),XBX(100),YBY(100)
DO 200 I=1,NA
XAX(I)=XA(I)
YAY(I)=YA(I)
200 CONTINUE
DO 201 I=1,NB
XBX(I)=XB(I)
YBY(I)=YBP(I)
201 CONTINUE
NAA=NA
NBB=NBB
CALL SPLINC(YAY,XAX,NAA,CA)
CALL SPLINC(YBY,XBX,NBB,CB)
K=0
Q=5.0
104 K=K+1
X(K)=0
CALL SPLINE(YAY,XAX,NAAX,CA,0,AY)
CALL SPLINE(YBY,XBX,NBB,CB,0,BY)
Y(K)=12.127-(AY-BY)
IF(Q.GE.10.0)GO TO 100
Q=Q+0.2
GO TO 104
100 IF(Q.GT.30.0)GO TO 102
Q=Q+0.1
GO TO 104
102 CALL LIN04(X,Y,K,S,DS,B,DB,R)
RETURN
END

SUBROUTINE SPLINE(X,Y,M,C,XINT,YINT)
DIMENSION X(100),Y(100),C(4,100)
IF(XINT-X(1))7,1,2
1 YINT=Y(1)
RETURN
2 K=1
3 IF(XINT-X(K+1))6,4,5
4 YINT=Y(K+1)
RETURN
5 K=K+1
IF(M-K)7,7,3
6 YINT=(X(K+1)-XINT)*(C(1,K)*(X(K+1)-XINT)**2+C(3,K))
YINT=YINT+(XINT-X(K))*(C(2,K)*(XINT-X(K)**2+C(4,K))
RETURN
7 TYPE 100
100 FORMAT(1H0,5X,'*** OUT OF RANGE FOR INTERPOLATION! ***')
CALL EXIT
END
SUBROUTINE SPLINC(X, Y, M, C)
DIMENSION X(100), Y(100), D(100), P(100), E(100), C(4, 100), A
1(100, 3), B(100), Z(100)
MM=M-1
DO 2 K=1, MM
D(K)=X(K+1) -X(K)
P(K)=D(K)/6.
2 E(K)=(Y(K+1) -Y(K))/D(K)
DO 3 K=2, MM
B(K)=E(K) -E(K-1)
A(1, 2)=-1.-D(1)/D(2)
A(1, 3)=D(1)/D(2)
A(2, 3)=P(2) -P(1)*A(1, 3)
A(2, 2)=2.*(P(1)+P(2)) -P(1)*A(1, 2)
A(2, 3)=A(2, 3)/A(2, 2)
B(2)=B(2)/A(2, 2)
DO 4 K=3, MM
A(K, 2)=2.* (P(K-1)+P(K)) -P(K-1)*A(K-1, 3)
B(K)=B(K) -P(K-1)*B(K-1)
A(K, 3)=P(K)/A(K, 2)
4 B(K)=B(K)/A(K, 2)
Q=D(M-2)/D(M-1)
A(M, 1)=1.+Q*A(M-2, 3)
A(M, 2)=-Q-A(M, 1)*A(M-1, 3)
B(M)=B(M-2) -A(M, 1)*B(M-1)
Z(M)=B(M)/A(M, 2)
MN=M-2
DO 6 I=1, MN
K=M-I
6 Z(K)=B(K) -A(K, 3)*Z(K+1)
Z(1)=-A(1, 2)*Z(2) -A(1, 3)*Z(3)
DO 7 K=1, MM
Q=1./(6.*D(K))
C(1, K)=Z(K)*Q
C(2, K)=Z(K+1)*Q
C(3, K)=Y(K)/D(K) -Z(K)*P(K)
7 C(4, K)=Y(K+1)/D(K) -Z(K+1)*P(K)
RETURN
END
SUBROUTINE OMIT
COMMON /PTS/XA(100),YA(100),XB(100),YB(100),YBS(100),YBP(100)
COMMON /NPTS/NA,NB

LNA=NA
Q=YA(2)-YA(1)
IF(Q.GT.0.0001)GO TO 11
LNA=LNA-1
DO 12 I=1,LNA
XA(I)=XA(I+1)
YA(I)=YA(I+1)
12 CONTINUE
NA=LNA
GO TO 13

LNB=NB
Q=YBP(2)-YBP(1)
IF(Q.GT.0.0001)GO TO 14
LNB=LNB-1
DO 15 I=1,LNB
XB(I)=XB(I+1)
YBP(I)=YBP(I+1)
15 CONTINUE
NB=LNB
GO TO 11

RETURN
END

SUBROUTINE DAYME
DIMENSION A(2)
CALL DATE(A)
CALL TIME(B)
TYPE 1,A,B
1 FORMAT(20X,'RUN ON:'5X,2A5,5X,A5)
RETURN
END
SUBROUTINE LIN04(X,Y,N,B,SDB,A,SDA,R)
DIMENSION X(N),Y(N)
DOUBLE PRECISION XI,YI,TOTAL,SUMX,SUMY,XBAR,YBAR,SUMU2,
SUMV2,DSM,SDB,DA,DSDA,DR,SIGX,SIGY,SUMUV
TOTAL=DBLE(FLOAT(N))
SUMX=0.0DO
SUMY=0.0DO
DO 1 I=1,N
XI=DBLE(X(I))
YI=DBLE(Y(I))
SUMX=SUMX+XI
SUMY=SUMY+YI
1 CONTINUE
XBAR=SUMX/TOTAL
YBAR=SUMY/TOTAL
SUMU2=0.0DO
SUMV2=0.0DO
SUMUV=0.0DO
DO 2 I=1,N
XI=DBLE(X(I))
YI=DBLE(Y(I))
SUMU2=SUMU2+(XI-XBAR)**2
SUMV2=SUMV2+(YI-YBAR)**2
SUMUV=SUMUV+(XI-XBAR)*(YI-YBAR)
2 CONTINUE
SIGX=DSQRT(SUMU2/(TOTAL-1.0DO))
SIGY=DSQRT(SUMV2/(TOTAL-1.0DO))
DB=SIGY/SIGX
DR=SUMUV/(DSQRT(SUMU2*SUMV2))
DSDA=DSDB*DSQRT((1.0DO-DR*DR)/TOTAL)
DA=YBAR-DB*XBAR
DSDA=SIGY*DSQRT(((1.0DO-DR)/TOTAL)*((2.0DO+XBAR*XBAR*(1.0DO+DR)/(SIGX*SIGX)))
B=SNGL(DB)
SDB=SNGL(DSDB)
A=SNGL(DA)
SDA=SNGL(DSDA)
R=SNGL(DR)
RETURN
END
Appendix D. FORTRAN IV Program for Calculation of Theoretical Isotope Patterns and Deconvolution of Overlapped Patterns

Most organometallic compounds contain polyisotopic metals, and hence the mass spectra of such molecules are characterized by clusters of closely grouped peaks having distinctive isotope patterns. A particular ionic species can be quickly identified if its corresponding isotope pattern can be recognized. Hence, it is important to know what type of isotope pattern to expect for a particular group of polyisotopic elements, and many procedures are available for calculating such theoretical patterns (157, 158, 159). However, it is not uncommon to find that some ionic species present in an organometallic mass spectrum have the same nominal m/e values, and the effect of this overlap is to add the intensities at these common mass values. Consequently, the set of peaks in an overlapped pattern will have relative abundances that are much different from those of a non-overlapped pattern. The obvious solution for this overlapping problem is high resolution, but it has been shown (160) that even high resolution is not
sufficient to separate superimposed isotope patterns that occur at high mass values (m/e > 600).

The method used in this study is in essence a heuristic deconvolution procedure, and is perhaps best illustrated by considering a simple example, the mass spectrum of stannane, SnH₄. Saalfeld and Svec (161) have studied the mass spectrum of this compound using a sample which had been prepared from the separated ¹²⁰Sn isotope. A bar graph showing the five ions, ¹²⁰SnH₄⁺₊ (n=0-4), that were observed in this spectrum is given in Figure D-1(a). If however, the stannane sample had been prepared from naturally occurring tin which has ten isotopes with abundances greater than 0.35%, then the resulting mass spectrum would appear as shown in Figure D-1(b). For comparison, the theoretical isotope pattern characteristic for tin species (in this case Sn⁺) is given in Figure D-1(c).

Clearly then, it is impossible to ascertain the abundance of each ion present in Figure D-1(b) from a simple inspection of the spectrum.

A solution to this overlapping problem may be obtained in the following manner. The intensity data for an overlapped isotope pattern consisting of n separate ion species may be represented by a set of linear simultaneous equations
FIGURE D-1
MASS SPECTRUM OF STANNANE
\[ a_{11}x_1 + a_{12}x_2 + \ldots + a_{1n}x_n = b_1 \\
\vdots \\
\vdots \\
\vdots \\
\vdots \\
a_{m1}x_1 + a_{m2}x_2 + \ldots + a_{mn}x_n = b_m \]

where \( x_n \) is the percentage contribution of the \( n \)th ion involved in the overlapped pattern, \\
\( a_{mn} \) is the theoretical peak height (ion intensity) of the \( n \)th ion for the \( m \)th peak (m/e value) and \( b_m \) is the observed peak height of the \( m \)th peak in the overlapped pattern.

In general, there are more peaks, \( m \), (m/e values) in an overlapped pattern than there are ionic species, \( n \), (i.e., there are more equations than unknowns) and therefore this is an overdetermined system of equations. For example, in the mass spectrum of stannane, Figure D-1(b), the overlapped pattern extends over the mass range 112 to 128 (\( m = 17 \)), while there are only five (\( n \)) contributing ionic species.

The set of equations [D-1] can be written in matrix notation as

\[ A \hat{x} = b \]  

Although there is no unique solution to an overdetermined system, it is possible to obtain an optimum solution, \( \hat{x} \).
using the least squares criterion (162), which is given by

\[ \hat{x} = (A^T A)^{-1} A^T b \]  \[ \text{(D-3)} \]

where \( A^T \) is the transpose of \( A \). Once values of \( \hat{x} \) have been obtained from equation [D-3], it is possible to calculate new values \( b' \) according to

\[ A \hat{x} = b' \]  \[ \text{(D-4)} \]

The agreement between \( b \) and \( b' \) is therefore a measure of the goodness of fit.

In the present work, calculations of this type were carried out on a DEC PDP-10 computer using the program listed below. This program initially calculated the theoretical isotope pattern for each input ion, and then, using these intensities, computed the best possible fit to the overlapped intensity data according to equation [D-3]. In practice, it was frequently not known exactly how many or what types of ions were present in a particular overlapped pattern. Consequently, logical ion types and combinations were tried, and that combination which gave the best fit was taken to represent the actual make up of the observed overlapped pattern.

This technique can be illustrated with the overlapped mass spectrum of stannane. The intensities for the over-
lapped pattern, as given in Figure D-1(b), were read into the program along with all of the possible combinations of the ions $\text{SnH}_n^+$ (n=0-4) taken two, three, and four at a time. The computed best fit results for each case are listed in Table D-1. It should be noted that: (i) better fits were obtained for ion combinations which included the two ions which contributed most to the overlapped pattern, namely $\text{Sn}^+$ and $\text{SnH}_3^+$, and (ii) a perfect fit was obtained when all five ions were included.
### TABLE D-1
Overlapped Results for Stannane

<table>
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<tr>
<th>Sn⁺</th>
<th>SnH⁺</th>
<th>SnH₂⁺</th>
<th>SnH³⁺</th>
<th>SnH⁴⁺</th>
<th>Root Mean Square Error</th>
<th>Average Error</th>
<th>Maximum Error</th>
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<td>SnH₃⁺</td>
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<td>Root Mean Square Error</td>
<td>Average Error</td>
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</tbody>
</table>
COMMON /ARAY/M(500),P(500),MOLMS
COMMON /ELMTS/XM(295),PX(295),NN(92),MMS(92)
COMMON /NORM/A(30,10),B(30),XP(10)
DIMENSION TITLE(8),MOVL(30),MT(500),PT(500),BT(30),BN(310),BCAL(30),BCALN(30),ERR(30),ALPHA(10,8)
CALL IFILE(2,'TABLE')
READ(2,200)(XM(I),PX(I),I=1,295)
200 FORMAT(2F)
READ(2,201)(NN(I),I=1,92)
201 FORMAT(23I)
READ(2,202)(MMS(I),I=1,92)
202 FORMAT(41)
CALL IFILE(1,'INFO')
101 READ(1,1)IOVLP
1 FORMAT(I)
IF(IOVLP.EQ.0)GO TO 100
READ(1,2)NION,MPIN,MINT
2 FORMAT(3I)
MRNGE=MPIN-MINT+1
MOV(1)=MINT
DO 3 I=2,MRNGE
MOV(I)=MOV(I-1)+1
3 CONTINUE
IONCT=0
TYPE 11
11 FORMAT(1H1)
CALL DAYME
100 READ(1,12)TITLE
12 FORMAT(8A5)
CALL IONPAT(PSUM,NPKS)
IF(IOVLP.NE.0)GO TO 102
TYPE 11
CALL DAYME
TYPE 13,TITLE
13 FORMAT(1H0,5X,'ISOTOPE PATTERN FOR:'5X,8A5/)
TYPE 30
30 FORMAT(1H0,10X,'NOMINAL'10X,'CALCULATED'10X,'PERCENTAGE
1'10X,'RELATIVE')
TYPE 31
31 FORMAT(11X,'MASS'12X,'PROBABILITY'2(10X,'ABUNDANCE')/)
PMAX=0.0
DO 32 I=1,NPKS
IF(PMAX.GE.P(I))GO TO 32
PMAX=P(I)
32 CONTINUE
FQR=100.0/PMAX
PCTSUM=0.0
DO 33 I=1,NPKS
  PCTP=(P(I)*100.0)/PSUM
  RELP=P(I)*FQR
  PCTSUM=PCTSUM+PCTP
  TYPE 34,M(I),P(I),PCTP,RELP
33 FORMAT(12X,I3,11X,E13.7,2(8X,F11.7))
CONTINUE
TYPE 36,PSUM,PCTSUM
36 FORMAT(1HO,15X,'TOTALS = 'F10.7,12X,F11.7)
TYPE 11
CALL DAYTME
TYPE 13,TITLE
TYPE 37,MOLMS
37 FORMAT(1HO,10X,'MOLECULAR MASS = 'I3//)
TYPE 15
5 FORMAT(5X,'NOMINAL'2X,'RELATIVE')
TYPE 16
6 FORMAT(6X,'MASS'3X,'ABUNDANCE/')
102 DO 17 I=1,NPKS
  MT(I)=M(I)
  PT(I)=P(I)
17 CONTINUE
IF(IOVLP .NE.0)GO TO 103
CALL GRAPHD(MT,PT,NPKS,100.0)
IF(IOVLP .EQ.0)GO TO 101
103 IONCT=IONCT+1
CALL FILL(MT,PT,NPKS,MOVL,MRNGE,IONCT)
DO 38 I=1,8
  ALPHA(IONCT,I)=TITLE(I)
38 CONTINUE
IF(IONCT.LT.NION)GO TO 100
BMAX=0.0
DO 18 I=1,MRNGE
  READ(1,4)BT(I)
4 FORMAT(F)
  IF(BMAX.GE.BT(I))GO TO 18
  BMAX=BT(I)
18 CONTINUE
TBT=100.0/BMAX
DO 19 I=1,MRNGE
  BN(I)=BT(I)*TBT
  B(I)=BN(I)
19 CONTINUE
CALL NORMAL(MRNGE,NION)
DO 22 I=1,NION
DO 222 J=1,8
TITLE(J)=ALPHA(I,J)
222 CONTINUE
   TYPE 23,I,TITLE,XP(I)
23 FORMAT(1H0,5X,'OVERLAPPED ION ('I2,') IS '8A5,'PERCENTAGE 
   LE = 'F9.4)
22 CONTINUE
   TYPE 21
21 FORMAT(1H0,10X,'CALCULATED (+++), AND OBSERVED (***) OV 
   LERLAPPED PATTERNS'/)
   TYPE 15
   TYPE 16
   BCALMX=0.0
   DO 24 I=1,MRNGE
   BCAL(I)=0.0
   DO 25 J=1,NION
   BCAL(I)=BCAL(I)+A(I,J)*XP(J)
25 CONTINUE
   IF(BCALMX.GE.BCAL(I))GO TO 24
   BCALMX=BCAL(I)
24 CONTINUE
   BNMLT=100.0/BCALMX
   RMS=0.0
   TERR=0.0
   ERRMX=0.0
   DO 26 I=1,MRNGE
   BCALN(I)=BCAL(I)*BNMLT
   ERR(I)=BCALN(I)-BN(I)
   RMS=RMS+ERR(I)*ERR(I)
   TERR=TERR+ABS(ERR(I))
   IF(ERRMX.GE.ABS(ERR(I)))GO TO 26
   ERRMX=ABS(ERR(I))
26 CONTINUE
   CALL OGRAPH(MOVL,BN,BCALN,MRNGE)
   RMS=SQR(T(RMS/FLOAT(MRNGE)))
   AVGER=TERR/FLOAT(MRNGE)
   TYPE 27,RMS,ERRMX,AVGER
27 FORMAT(1H0,10X,'RMSERR = 'F10.5,5X,'MAXERR = 'F10.5,5X,'A 
   LVGERR = 'F10.5//' )
GO TO 101
STOP
END
SUBROUTINE IONPAT(PSUM,NPKS)
COMMON /ARRAY/M(500),P(500),MOLMS
COMMON /ELMTS/XM(295),PX(295),NN(92),MMS(92)
DIMENSION MTEMP(10),PTEMP(10),MT(500)
DOUBLE PRECISION DP(500),PT(500),DPSUM
NPKS=1
MT(1)=0
PT(1)=1.0D0
MOLMS=0
READ(1,1)NOAT
1 FORMAT(I)
INOAT=0
80 READ(1,2)IELNO,NOEL
2 FORMAT(2I)
CALL LIST(MTEMP,PTEMP,N,IELNO)
DO 10 I=1,NOEL
NTPKS=0
DO 11 J=1,NPKS
DO 12 K=1,N
NTPKS=NTPKS+1
M(NTPKS)=MT(J)=MTEMP(K)
DP(NTPKS)=PT(J)*DBLE(PTEMP(K))
12 CONTINUE
11 CONTINUE
CALL SHRINK(DP,NPKS,NTPKS)
INOAT=INOAT+1
DO 13 II=1,NPKS
MT(II)=M(II)
13 PT(II)=DP(II)
MOLMS=MOLMS+MMS(IELNO)
10 CONTINUE
IF(INOAT.LT.NOAT)GO TO 80
DPSUM=0.0D0
DO 14 I=1,NPKS
DPSUM=DPSUM+DP(I)
P(I)=SNGL(DP(I))
14 CONTINUE
PSUM=SNGL(DPSUM)
RETURN
END
SUBROUTINE LIST(M,P,N,IELNO)
COMMON /ELMTS/XM(295),PX(295),NN(92),MMS(92)
DIMENSION M(10),P(10)
IELNO=IELNO-1
NSUM=0
IF (IELNO.EQ.0) GO TO 14
DO 15 I=1,IELNO
15 NSUM=NSUM+NN(I)
14 N=NN(I)
DO 16 I=1,N
M(I)=XM(NSUM+I)=0.5
P(I)=PX(NSUM+I)
IF (P(I)) 17,16,16
16 CONTINUE
RETURN
17 TYPE 18
18 FORMAT(1H0,10X,'ELEMENT CHOSEN IS RADIOACTIVE'//)
CALL EXIT
END

SUBROUTINE SHRINK(DP,NPKS,NTPKS)
COMMON /ARAY/M(500),P(500),MOLMS
DIMENSION MT(500)
DOUBLE PRECISION DP(500),PT(500)
IMAX=1
IMIN=1000
DO 91 I=1,NTPKS
IF (M(I).GE.IMIN) GO TO 92
IMIN=M(I)
92 IF (M(I).LE.IMAX) GO TO 91
IMAX=M(I)
91 CONTINUE
NPKS=IMAX-IMIN+1
MT(1)=IMIN
DO 93 I=2,NPKS
MT(I)=MT(I-1)+1
DO 10 I=1,NPKS
PT(I)=0.0D0
11 DO 10 J=1,NTPKS
IF (MT(I).NE.M(J)) GO TO 11
PT(I)=PT(I)+DP(J)
10 CONTINUE
RETURN
93 CONTINUE
CONTINUE
DO 22 I=1,NPKS
M(I)=MT(I)
DP(I)=PT(I)
RETURN
END

SUBROUTINE GRAPH(M,P,N,HI)
DIMENSION M(500),P(500),IP(500),ILINE(100),PN(500)
DATA IBLK,IAST/1H,1H*/
PMAX=0.0
DO 20 I=1,N
IF(PMAX.GE.P(I))GO TO 20
PMAX=P(I)
CONTINUE
AJUST=HI/PMAX
DO 21 I=1,N
PN(I)=P(I)*AJUST
IP(I)=PN(I)+0.5
CONTINUE
LEFT=N
DO 12 I=N,1,-1
IF(IP(I)-1).LT.13,13,14
CONTINUE
DO 16 I=1,LEFT
L=IP(I)
DO 17 J=1,100
ILINE(J)=IBLK
CONTINUE
RETURN
END
SUBROUTINE FILL(MT,PT,NPKS,MVOL,MRNGE,IONCT)
COMMON /NORM/A(30,10),B(30),XP(10)
DIMENSION MT(500),PT(500),MVOL(30),PN(500)
PMAX=0.0
DO 10 I=1,NPKS
  IF(PMAX.GE.PT(I)) GO TO 10
  PMAX=PT(I)
10 CONTINUE
  T=100.0/PMAX
DO 11 I=1,NPKS
  PN(I)=PT(I)*T
11 CONTINUE
          DO 12 I=1,MRNGE
            A(I,IONCT)=0.0
            DO 13 J=1,NPKS
              IF(MVOL(I).NE.MT(J)) GO TO 13
              A(I,IONCT)=PN(J)
13 CONTINUE
12 CONTINUE
RETURN
END

SUBROUTINE OGRAPH(M,O,C,N)
DIMENSION M(30),O(30),C(30),IO(100),IC(100),ILO(100),ILC(100)
DATA IBLK,IAST,IPLS/LH ,1H*,1H+/ DO 10 I=1,N
  IO(I)=O(I)+0.5
  IC(I)=C(I)+0.5
10 CONTINUE
          DO 11 I=1,N
            L=IO(I)
            K=IC(I)
            DO 12 J=1,100
              ILO(J)=IBLK
12 ILC(J)=IBLK
11 CONTINUE
            DO 13 J=1,L
13 ILO(J)=IAST
14 CONTINUE
            ILC(J)=IPLS
TYPE 15,M(I),O(I),ILO
SUBROUTINE NORMAL(M,N)
COMMON /NORM/A(30,10),B(30),XP(10)
DOUBLE PRECISION AD(30,10),AT(10,30),BD(30),C(10,10),DC(10)
DOUBLE PRECISION X(10),XSUM,UL(10,10),DIGITS
DIMENSION IPS(10)
DO 10 I=1,M
DO 11 J=1,N
AD(I,J)=DBLE(A(I,J))
AT(J,I)=AD(I,J)
11 CONTINUE
BD(I)=DBLE(B(I))
10 CONTINUE
DO 12 I=1,N
DO 13 K=1,N
C(I,K)=0.0D0
DO 14 J=1,M
C(I,K)=C(I,K)+AT(I,J)*AD(J,K)
14 CONTINUE
13 CONTINUE
DC(I)=0.0D0
DO 15 L=1,M
DC(I)=DC(I)+AT(I,L)*BD(L)
15 CONTINUE
12 CONTINUE
CALL DECOMP(N,C,UL,IPS)
CALL SOLVE(N,UL,DC,X,IPS)
CALL IMPRUV(N,C,UL,DC,X,DIGITS,IPS)
CALL QUAD(C,X,M,N)
XSUM=0.0D0
DO 16 I=1,N
XSUM=XSUM+X(I)
16 CONTINUE
DO 17 I=1,N
17 XP(I)=SNGL(X(I)*100.0D0/XSUM)
RETURN
END

SUBROUTINE DECOMP(NN,A,UL,IPS)
DOUBLE PRECISION A(10,10),UL(10,10),SCALES(10),ROWNRM,BIG,SIZE
DOUBLE PRECISION PIVOT,EM
DIMENSION IPS(10)
N=NN
DO 5 I=1,N
IPS(I)=I
ROWNRM=0.0D0
DO 2 J=1,N
UL(I,J)=A(I,J)
IF(ROWNRM-DABS(UL(I,J)))1,2,2
1 ROWNRM=DABS(UL(I,J))
2 CONTINUE
IF(ROWNRM)3,4,3
3 SCALES(I)=1.0D0/ROWNRM
GO TO 5
4 CALL SING(1)
SCALES(I)=0.0D0
5 CONTINUE
NM1=N-1
DO 17 K=1,NM1
BIG=0.0D0
DO 11 I=K,N
IP=IPS(I)
SIZE=DABS(UL(IP,K))*SCALES(IP)
IF(SIZE-BIG)11,11,10
10 BIG=SIZE
IDXPIV=I
11 CONTINUE
IF(BIG)13,12,13
12 CALL SING(2)
GO TO 17
13 IF(IDXPIV-K)14,15,14
14 J=IPS(K)
IPS(K)=IPS(IDXPIV)
IPS(IDXPIV)=J
SUBROUTINE SOLVE(NN,UL,B,X,IPS)  
DOUBLE PRECISION UL(10,10),B(10),X(10),SUM  
DIMENSION IPS(10)  
N=NN  
NP1=N+1  
IP=IPS(1)  
X(1)=B(IP)  
DO 2 I=2,N  
IP=IPS(I)  
IM1=I-1  
SUM=0.0DO  
DO 1 J=1,IM1  
1 SUM=SUM+UL(IP,J)*X(J)  
2 X(I)=B(IP)-SUM  
IP=IPS(N)  
X(N)=X(N)/UL(IP,N)  
DO 4 IBACK=2,N  
I=NP1-IBACK  
IP=IPS(I)  
IP1=I+1  
SUM=0.0DO  
DO 3 J=IP1,N  
3 SUM=SUM+UL(IP,J)*X(J)  
4 X(I)=(X(I)-SUM)/UL(IP,I)
RETURN
END

SUBROUTINE IMPRUV(NN, A, UL, B, X, DIGITS, IPS)
DOUBLE PRECISION A(10, 10), UL(10, 10), B(10), X(10), R(10),
1DX(10), EPS
DOUBLE PRECISION XNORM, DIGITS, SUM, DXNORM, T
DIMENSION IPS(10)
N=NN
EPS=1.0D-16
ITMAX=32
XNORM=0.0D0
DO 1 I=1, N
1 XNORM=DMA1(XNORM, DABS(X(I)))
   IF(XNORM).LT.3.2D3
2 DIGITS=-DB10(EPS)
   GO TO 10
3 DO 9 ITER=1, ITMAX
4 SUM=SUM+A(I,J)*X(J)
5 R(I)=SUM
   CALL SOLVE(N, UL, R, DX, IPS)
   DXNORM=0.0D0
6 DO 8 I=1, N
7 T=X(I)
   X(I)=X(I)+DX(I)
   DXNORM=DMA1(DXNORM, DABS(X(I)-T))
   CONTINUE
   IF(ITER-1).LT.7,8
7 DIGITS=-DB10(DMA1(DXNORM/XNORM, EPS))
8 IF(DXNORM-EPS*XNORM).LE.10,10,9
9 CONTINUE
   CALL SING(3)
10 RETURN
END
SUBROUTINE SING(IWHY)
   GO TO (1,2,3),IWHY
1   TYPE 11
11  FORMAT(1H0,10X,'MATRIX WITH ZERO ROW IN DECOMPOSE'/)
   GO TO 10
2   TYPE 12
12  FORMAT(1H0,10X,'SINGULAR MATRIX IN DECOMPOSE. ZERO DIV
   LIDE IN SOLVE'/)
   GO TO 10
3   TYPE 13
13  FORMAT(1H0,10X,'NO CONVERGENCE IN IMPRUV MATRIX IS NEAR
   LY SINGULAR'/)
10  RETURN
END

SUBROUTINE DAYTIME
DIMENSION A(2)
CALL DATE(A)
CALL TIME(B)
TYPE 1,A,B
1  FORMAT(20X,'RUN ON:'5X,2A5,5X,A5)
RETURN
END

SUBROUTINE QUAD(C,X,M,N)
COMMON /NORM/A(30,10),B(30),XP(10)
DOUBLE PRECISION AD(30,10),BD(30),C(10,10),X(10),BDT(1,
130),BB(1,10),XK(10,0/100),SUM1,SUM2,W(10,101),E(10)
DO 1 I=1,M
   DO 2 J=1,N
      AD(I,J)=DBLE(A(I,J))
2    CONTINUE
      BD(I)=DBLE(B(I))
      BDT(1,I)=BD(I)
1    CONTINUE
   DO 3 I=1,N
      BB(1,I)=0.0D0
DO 4 J=1,M
  BB(1,I)=BB(1,I)+BDT(1,J)*AD(J,I)
4  CONTINUE
3  CONTINUE
  K=0
DO 9 I=1,N
  XK(I,K)=X(I)
9  CONTINUE
17 DO 10 I=1,N
  SUM1=0.0D0
  SUM2=0.0D0
  IF(K.EQ.0)GO TO 11
  IM1=I-1
  IF(IM1.EQ.0)GO TO 11
  DO 12 J=1,IM1
    SUM1=SUM1+C(I,J)*XK(J,K+1)
12  CONTINUE
11 IF(I.EQ.N)GO TO 13
  DO 14 J=I+1,N
    SUM2=SUM2+C(I,J)*XK(J,K)
14  CONTINUE
13 W(I,K+1)=(-1.0D0/C(I,I))*(SUM1+SUM2-BB(1,I)/2.0D0)
  XK(I,K+1)=DMAX1(0.0D0,W(I,K+1))
10 CONTINUE
  K=K+1
  IF(K.GT.100)GO TO 15
  L=0
DO 16 I=1,N
  E(I)=DABS(XK(I,K-1)-XK(I,K))
  IF(E(I).LE.1.0D-12)L=L+1
16 CONTINUE
  IF(L.EQ.N)GO TO 15
  GO TO 17
15 DO 18 I=1,N
  X(I)=XK(I,K)
18 CONTINUE
RETURN
END
Appendix E.  Graphical Determination of Metastable Masses
and FORTRAN IV Program for the Calculation of
Metastable Transitions

The majority of ions formed by electron impact are
either stable with insufficient excitation energy to decompose,
or unstable with adequate energy to decompose before leaving
the ionization chamber. However, some ions have a half-life
that is sufficiently long to allow them to be accelerated out
of the ionization chamber, but decompose in transit to the
magnetic analyzer. Such an in-flight fragmentation is known
as a metastable transition where a parent ion of mass \( m_1 \),
decomposes into a stable fragment ion of mass \( m_2 \), and a neutral
particle of mass \( m_3 \).

\[
    m_1^+ \rightarrow m_2^+ + m_3
\]  \[\text{[E-1]}\]

The process is characterized by a broad, low intensity,
diffuse peak appearing at an apparent mass, \( m^* \), given by

\[
    m^* = \frac{m_2^2}{m_1}
\]  \[\text{[E-2]}\]

A reproduction of part of the mass spectrum for the compound
\((\text{CH}_3)_3\text{Si-Mn(OC)}_5\) illustrating a typical metastable between
two normal peaks of masses \( M_1 \) and \( M_2 \) \((M_2 = M_1 + 1)\) is given
In Figure E-1.

In a magnetic deflection mass spectrometer the m/e in register is given by the expression

\[
\frac{m}{e} = \frac{H^2 r^2}{2 V c^2} \quad [E-3]
\]

where \( m \) is the mass in atomic mass units
\( e \) is the number of electronic charges
\( H \) is the magnetic field strength in gauss
\( r \) is the radius of curvature in cm
\( V \) is the accelerating potential in volts

and \( c \) is the velocity of light

With \( r \) and \( V \) fixed, the mass-to-charge ratio is scanned by a linear variation with time of the current flowing through the coils of the electromagnet. However, the resulting magnetic field strength is not entirely linear with time due to hysteresis effects. For the small change in magnetic field strength required to scan from mass \( M_1 \) to mass \( M_2 \), it may be assumed that \( H \) is linear with time. Ion intensities, as displayed on a strip chart recorder, are also a linear function of time. Therefore, graphical distances are directly proportional to \( H \), and according to equation \([E-3]\) are also \( \frac{1}{2} \) directly proportional to \( m^2 \). In general then
FIGURE E-1
A METASTABLE PEAK
\[ L = \alpha \frac{1}{m^1} \]  

where \( L \) represents a graphical distance representing a small change in \( H \)

\( \alpha \) is a constant of proportionality

and \( m \) represents the mass-to-charge ratio

Differentiating equation \([E-4]\) yields

\[ \frac{dL}{dm} = \frac{\alpha}{2 \ m^{\frac{1}{3}}} \]  

\[ [E-5] \]

Let the mass of the metastable be \( M \), and the distance measured between \( M_1 \) and the apex of the metastable be represented by "b" as indicated in Figure E-1. Integrating equation \([E-5]\) between these limits gives

\[ \int_{0}^{b} dL = b = \int_{M_1}^{M} \frac{\alpha \ dm}{2 \ m^{\frac{1}{3}}} = \alpha (M^{\frac{1}{3}} - M_1^{\frac{1}{3}}) \]  

\[ [E-6] \]

With the measured distance between \( M_1 \) and \( M_2 \) represented by "a", a similar integration gives

\[ \int_{0}^{a} dL = a = \int_{M_1}^{M_2} \frac{\alpha \ dm}{2 \ m^{\frac{1}{3}}} = \alpha (M_2^{\frac{1}{3}} - M_1^{\frac{1}{3}}) \]  

\[ [E-7] \]

Dividing equation \([E-6]\) by \([E-7]\) and rearranging yields

\[ M = \left[ \frac{(a - b)M_1^{\frac{1}{3}} + b M_2^{\frac{1}{3}}}{a} \right]^2 \]  

\[ [E-8] \]
Once the metastable mass has been determined, transitions can be found by the trial-and-error method of inserting $m_1$ and $m_2$ values into equation [E-2]. Due to the many combinations of $m_1$ and $m_2$ that can yield approximately the same $m^*$, this process is by no means routine. To facilitate this analysis the following computer program was written which, for a given metastable, calculates all mathematically possible transitions for this peak subject to certain constraints which appear as input data to the program.

A DEC PDP-10 computer was programmed with the following input data: (i) the m/e and corresponding intensities of all normal peaks in the spectrum (each normal peak is assumed to be an integer); (ii) values for $M_1$, $M_2$, $a$, and $b$ according to Figure E-1; and (iii) a range of error, an arbitrary value depending upon the readability of the observed metastable.

The computer was then instructed to derive and print the metastable transition [E-1] from the relationship [E-2] subject to the following conditions: (i) $m^*$ calculated must fall within $M$ calculated $\pm$ range of error; (ii) for a $m^*$ which satisfies (i), $m_1$ and $m_2$ must appear in the list of $m_i$; and (iii) $m_1$ and $m_2$ must have intensities $> 0.1\%$ of the most intense peak.
In practice, with an error range of ± 0.2 m/e, the number of transitions listed by the computer averaged about 10. The most likely transition was then selected from this output.

For the metastable illustrated in Figure E-1, the nominal masses \( M_1 \) and \( M_2 \) were 27 and 28, and the measured distances \( a \) and \( b \) were 2.675" and 2.056" respectively. Using equation [E-8], the metastable peak was calculated to have a m/e value of 27.77. Upon examination of the list of possible transitions tabulated by the computer, the most logical one was

\[
(CH_3)_3Si^+ \rightarrow CH_3SiH_2^+ + C_2H_4 \quad [E-9]
\]

This particular metastable transition has also been observed in the mass spectrum of \((CH_3)_4Si\) (70).

```plaintext
DIMENSION TITLE(15),LYNE(15),A(2)
COMMON /MASS/M(600),X(600),NP
CALL IFILE(1,'MASS')
CALL IFILE(2,'METM')
READ(1,22)TITLE
22 FORMAT(15A5)
READ(1,22)LYNE
I=0
XMAX=0.0
4 I=I+1
READ(1,1)IM,ABN
1 FORMAT(I,F)
IP(IM)2,2,3
3 M(I)=IM
```
X(I)=ABN
IF(XMAX.GE.X(I))GO TO 4
XMAX=X(I)
GO TO 4
2   NP=I
   FAC=100.0/XMAX
   DO 5 I=1,NP
   X(I)=X(I)*FAC
5   CONTINUE
100  TYPE 11
11   FORMAT(1H1)
   CALL DATE(A)
   CALL TIME(B)
   TYPE 12,A,B
12   FORMAT(20X,'RUN ON:'5X,2A5,5X,A5)
   READ(2,6)IFUL,MAX,MIN
6   FORMAT(3I)
   READ(2,111)Q,R,S,T,ERROR
111  FORMAT(5F)
   TYPE 23,TITLE
23   FORMAT(1HO,10X,'COMPOUND:'15A5)
   TYPE 24,LYNE
24   FORMAT(1HO,10X,'CONDITIONS:'5X,15A5)
   TYPE 122
122  FORMAT(1HO,10X,'METASTABLE MASS DETERMINATION AND ANALYSIS:'/)
   TYPE 133,Q,R
133  FORMAT(1HO,10X,'MASSES:'5X,'M(1)='F10.5,5X,'M(2)='F10
1.5)
   TYPE 144,S,T
144  FORMAT(1HO,10X,'DISTANCES:'8X,'A='F6.3,6X,'B='F6.3)
   Z=((S-T)*SQRT(Q)+(T*SQRT(R))/S)**2
   TYPE 155,Z
155  FORMAT(1HO,10X,'METASTABLE MASS =''F10.5/)
   TYPE 166,ERROR
166  FORMAT(1HO,10X,'CALCULATED BEST COMBINATIONS FOR ERROR
LIMITS OF ABS('F7.5,'))
   IF(IFUL.EQ.0)GO TO 167
   TYPE 168
168  FORMAT(1HO,10X,'INCLUDING THE CONSTRAINT OF A FULL LIST
SEARCH'/)
167  TYPE 177
177  FORMAT(1HO,15X,'M(1) ''5X,'M(2) ''5X,'M5' ''5X,'NEUTRAL'5X,'E
1RROR'/)
IPNT=0
ICNT=0
K=MIN+1
DO 188 I=K,MAX
L=I-1
DO 199 J=MIN,L
XM=FLOAT(J*J)/FLOAT(I)
ERR=XM-Z
IF(ABS(ERR).GT.ERROR)GO TO 199
IF(IFUL.EQ.0)GO TO 200
CALL SRCH(I,J,IPNT)
IF(IPNT.EQ.0)GO TO 199
200 ICNT=ICNT+1
IX=(ICNT-36)/60
IF((IX*60+36).EQ.ICNT)TYPE 11
NEUT=I-J
TYPE 20,I,J,XM,NEUT,ERR
20 FORMAT(15X,14,5X,14,4X,F7.3,3X,14,6X,F7.4)
199 CONTINUE
188 CONTINUE
GO TO 100
STOP
END

SUBROUTINE SRCH(M1,M2,IPNT)
COMMON /MASS/M(600),X(600),NP
IPNT=0
I1=0
I2=0
L=0
DO 10 I=1,NP
L=L+1
IF(M2.NE.M(I))GO TO 10
IF(X(I).LE.0.1)GO TO 10
I2=1
GO TO 11
10 CONTINUE
11 IF(I2.EQ.0)GO TO 12
L=L+1
DO 13 I=L,NP
IF(M1.NE.M(I))GO TO 13
IF(X(I).LE.0.1)GO TO 13
I1=1
GO TO 14
13 CONTINUE
14 IF((I2.EQ.1).AND.(I1.EQ.1))IPNT=1
12 RETURN
END
Appendix F. Internal Pressure Calculation for the Effusion Reactor

Under molecular flow conditions the conductance of an orifice is given by (30)

\[ F = \frac{1}{4} u A \]  \hspace{1cm} [F-1]

where \( u \) is the average molecular velocity

and \( A \) is the area of the orifice

This relation is only applicable to orifices having an infinitely small thickness. The actual experimental conditions approximate this, since the reactor orifice is contained in a platinum foil only 0.0051 cm thick. The orifice radius is 0.0444 cm which results in an area of \( 6.21 \times 10^{-3} \text{ cm}^2 \).

From the kinetic theory of gases, the average molecular velocity is

\[ u = \left( \frac{8 R T}{\nu M} \right)^{\frac{1}{2}} \]  \hspace{1cm} [F-2]

where \( R \) is the gas constant

\( T \) is the absolute temperature

and \( M \) is the molecular weight of the gas
If the gas in the reactor has a molecular weight of 100, then the average molecular velocity at a temperature of 1000\(^\circ\)K is \(4.60 \times 10^4\) cm/sec. Therefore the orifice in the molecular flow reactor has a conductance of \(7.14 \times 10^{-2}\) litres/sec.

The law of conductance for a gas flowing through an orifice is given by (32)

\[
Q = F(p_2 - p_1) \tag{F-3}
\]

where \(Q\) is the flow of molecules through the orifice

\(F\) is the conductance of the orifice

\(p_2\) is the internal reactor pressure

and \(p_1\) is the pressure outside the reactor.

In the mass spectrometer, the pressure outside the reactor, \(p_1\), is typically of the order of \(10^{-7}\) torr (i.e. \(p_1 \ll p_2\)) and hence equation [F-3] becomes

\[
Q = 7.14 \times 10^{-2} \times p_2 \tag{F-4}
\]

Clearly, if \(Q\) is known, then the internal pressure of the cell may be calculated.

Gas flows into the reactor through a tube which is connected to an external reservoir via a precision gas metering valve. The flow of gas through this valve must also obey equation [F-3], and in this case

\[
Q' = F'(p_2' - p_1') \tag{F-5}
\]
where \( Q' \) is the flow of molecules through the valve
\( F' \) is the conductance of the valve
\( p_2' \) is the external reservoir pressure
and \( p_1' \) is the pressure downstream from the valve.

Typical settings for the gas metering valve used in this study result in a conductance for this device of approximately \( 10^{-6} \) litres/sec (31). Initially the pressure in the external storage bulb was 500 torr, and therefore \( p_1' \ll p_2' \). Hence the flow of molecules through the valve, \( Q' \), is \( 5 \times 10^{-4} \) l-torr/sec. Neglecting the conductance of the connecting tube, then \( Q' \) is also the rate of flow of gas into the reactor. Assuming that the flow of molecules out of the reactor equals the flow of molecules into the reactor, i.e. \( Q' = Q \), then the internal reactor pressure, \( p_2 \), is \( 7 \times 10^{-3} \) torr. Thus Knudsen effusion occurs under these conditions.

It should be pointed out that the conductance for the metering valve was given for a pressure differential of 1 atmosphere. In this case the differential across the valve was less than 1 atm., and hence the valve's resulting conductance would be somewhat lower. Also, the conductance of the tube leading from the valve to the reactor was neglected. The inclusion of these factors would tend to lower the final value obtained for \( Q' \). Therefore, the value
calculated for the internal pressure of the reactor may be viewed as an upper limit.
Appendix G. Estimation of the Ionization Potential of the Trimethylplumbyl Radical

If the value for the appearance potential of the ion Me₃Pb⁺ from tetramethyllead represents the energy required for this process

\[ \text{Me}_4\text{Pb} + e \rightarrow \text{Me}_3\text{Pb}^+ + \text{Me}^* + 2e \]  \[ \text{[G-1]} \]

then use of equation [A-4] gives

\[ D(\text{Me}_3\text{Pb-Me}) = A(\text{Me}_3\text{Pb}^+) - I(\text{Me}_3\text{Pb}^*) \]  \[ \text{[G-2]} \]

Clearly, the ionization potential of the trimethylplumbyl radical may be obtained from equation [G-2] if: (i) the appearance potential of Me₃Pb⁺ from Me₄Pb is known, and (ii) the energy required to break the first methyl-lead bond in Me₄Pb, D(Me₃Pb-Me), is known.

Two separate determinations of A(Me₃Pb⁺) from Me₄Pb have been previously reported. Hobrock and Kiser obtained a value of 8.9 ± 0.1 eV (124), while de Ridder and Dijkstra obtained a value of 10.1 ± 0.3 eV (70). Since these two values differ substantially, this same appearance potential was redetermined in an independent study in this laboratory. The average of eight individual determinations gave a value
of 8.78 eV with a standard deviation of 0.12 eV, in good agreement with Hobrock and Kiser's measurement.

A value for \( D(\text{Me}_3\text{Pb-Me}) \) can be approximated from a thermochemical consideration of the tetramethyl compounds of Group IVB. In \( \text{Me}_4\text{M} \) (\( \text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb} \)) there are four metal-methyl bonds, and the average bond dissociation energy, \( E(\text{Me-M}) \), is defined as one quarter of the total enthalpy required to break all of the methyl-metal bonds in \( \text{Me}_4\text{M} \). This disruption process may be written as

\[
\text{Me}_4\text{M}(g) \rightarrow 4\text{Me} \cdot (g) + \text{M}(g) \quad \text{[G-3]}
\]

for which

\[
E(\text{Me-M}) = \frac{1}{4}[\Delta H^0_f(\text{M}(g)) + 4\Delta H^0_f(\text{Me} \cdot (g)) - \Delta H^0_f(\text{Me}_4\text{M}(g))] \quad \text{[G-4]}
\]

The relevant heats of formation are listed in Table G-1, and the calculated average bond dissociation energies for the tetramethyl compounds are listed in Table G-2.

Also listed in Table G-2 are the values obtained by Lappert et al. (123) for the bond dissociation energies, \( D(\text{Me}_3\text{M-Me}) \), corresponding to the cleavage of the first methyl group in \( \text{Me}_4\text{M} \) (\( \text{M} = \text{Si}, \text{Ge}, \text{Sn} \)). It should be pointed out that in every case: (i) the values \( D(\text{Me}_3\text{M-Me}) \) are greater than the corresponding average bond dissociation energies, \( E(\text{Me-M}) \), and (ii) the quantity \( (D-E) = \Delta \) is a constant
TABLE G-1

Heats of Formation for the Molecules, Atoms, and the Radical Used in Thermochemical Calculations

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^o_f$ (kcal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$^-$</td>
<td>33.2 ± 1.0</td>
<td>125</td>
</tr>
<tr>
<td>Si</td>
<td>108.9 ± 0.5</td>
<td>125</td>
</tr>
<tr>
<td>Ge</td>
<td>90.0 ± 0.5</td>
<td>125</td>
</tr>
<tr>
<td>Sn</td>
<td>72.2 ± 0.5</td>
<td>125</td>
</tr>
<tr>
<td>Pb</td>
<td>46.6 ± 0.5</td>
<td>125</td>
</tr>
<tr>
<td>Me$_4$Si</td>
<td>-33.0 ± 2.0</td>
<td>126</td>
</tr>
<tr>
<td>Me$_4$Ge</td>
<td>-20.7 ± 2.0</td>
<td>127</td>
</tr>
<tr>
<td>Me$_4$Sn</td>
<td>-4.6 ± 0.6</td>
<td>128</td>
</tr>
<tr>
<td>Me$_4$Pb</td>
<td>32.6 ± 0.3</td>
<td>129</td>
</tr>
</tbody>
</table>
TABLE G-2
Bond Dissociation Energies for the Tetramethyl Compounds of Group IVB

<table>
<thead>
<tr>
<th>Molecule Me₄M</th>
<th>E(Me-M) kcal/mole</th>
<th>D(Me₃M-Me) kcal/mole</th>
<th>Δ = (D-E) kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>68.7 ± 1.6</td>
<td>74.3 ± 4.6</td>
<td>5.6 ± 6.2</td>
</tr>
<tr>
<td>Ge</td>
<td>60.9 ± 1.6</td>
<td>67.8 ± 3.2</td>
<td>6.9 ± 4.8</td>
</tr>
<tr>
<td>Sn</td>
<td>52.4 ± 1.3</td>
<td>61.1 ± 4.4</td>
<td>8.7 ± 5.7</td>
</tr>
<tr>
<td>Pb</td>
<td>36.7 ± 1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
within the error limits.

For the compounds Me₄M (M = Si, Ge, Sn), the average value of the quantity (D-E) = Δ was found to be \( \Delta_{\text{avg}} = 7.1 \pm 6.2 \) kcal/mole. Therefore, a reasonable approximation for the energy required to break the first methyl-lead bond in tetramethyllead is given by

\[
D(\text{Me}_3\text{Pb-Me}) = E(\text{Me-Pb}) + \Delta_{\text{avg}} \quad \text{[G-5]}
\]

for which \( D(\text{Me}_3\text{Pb-Me}) = 36.7 + 7.1 = 43.8 \pm 7.4 \) kcal/mole.

It should be noted that this type of approximation has been found to be quite good in estimating bond dissociation energies in other Group IVB compounds (130, 132).

The ionization potential of the trimethylplumbyl radical can now be estimated by substituting the values obtained for \( A(\text{Me}_3\text{Pb}^+) \) from Me₄Pb and \( D(\text{Me}_3\text{Pb-Me}) \) into equation [G-2] to give \( I(\text{Me}_3\text{Pb}^-) = 202.6 - 43.8 = 158.8 \pm 10.1 \) kcal/mole = 6.89 \pm 0.44 ev.

During the preparation of this manuscript, appearance potential measurements became available (163) which allowed the ionization potential of the \( \text{Me}_3\text{Pb}^- \) radical to be calculated as 6.64 \pm 0.43 eV, in excellent agreement with the estimate derived in this work.