

IONIZATION AND FRAGMENTATION OF DIMETHYLZINC, TRIMETHYLALUMINUM, AND TRIMETHYLANTIMONY*

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INTRODUCTION

In recent years the ionization and subsequent dissociation of several methyl-substituted metal compounds have been investigated by mass spectrometric techniques. These studies demonstrate the effect of the central metal atom upon: (i) the ionization potential of the molecule; (ii) the appearance potentials of the various fragment ions; and (iii) the cracking patterns of the molecules [extent of hydrogen atom rearrangement, intensities of $M(\text{CH}_3)_x^+$ ions, etc.]

The mass spectra of and the metastable transitions which occur in a number of $M(\text{CH}_3)_x$ type molecules have been reported previously by Dibeler and associates¹⁻³. Hobrock and Kiser⁴ have studied the ions formed from the group IVA tetramethyl compounds upon electron bombardment. Trimethylboron has been investigated mass spectrometrically⁵⁻⁷; however, no reports upon the trimethyl compounds of the remaining group IIIA elements have been made. In group VA, the $M(\text{CH}_3)_3$ molecules, where M is nitrogen^{8,9}, phosphorus¹⁰, or arsenic¹¹, have been studied.

The purpose of this paper is to extend the existing information upon the electron impact phenomena of $M(\text{CH}_3)_x$ molecules by presenting mass spectrometric data obtained in our laboratory for dimethylzinc, trimethylaluminum, and trimethylantimony. In addition, ionization potentials of several $M(\text{CH}_3)_x$ radicals and molecules are estimated from experimental data obtained in this study and other reported data.

EXPERIMENTAL

The mass spectra and appearance potentials were determined with a Bendix model 12-100 time-of-flight mass spectrometer equipped with a room temperature inlet system. The instrumentation has been described previously¹².

The experimental ionization efficiency curves for the positive ions studied were interpreted using the extrapolated voltage differences method¹³ and the method

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of Lossing, Tickner, and Bryce¹⁴. Krypton or xenon mixed with the compounds being investigated was used to calibrate the ionizing voltage scale. Spectroscopic values¹⁵ for the ionization potentials of krypton (14.00 eV) and xenon (12.13 eV) were employed for this purpose.

The samples of dimethylzinc, trimethylaluminum, and trimethylantimony were obtained from commercial sources. Trimethylantimony was obtained as a 25% by weight solution of the metal alkyl in n-heptane solvent. Removal of the solvent was found unnecessary since the n-heptane mass spectrum¹⁶ did not interfere with the metal-containing ions in the mass spectrum of trimethylantimony. Low voltage mass spectrometry indicated no volatile impurities in dimethylzinc and trimethylaluminum.

Decomposition products were repeatedly cleaned from the ion source and the Wiley magnetic electron multiplier components throughout this study. Also, frequent replacements of the tungsten filament were necessary. The mass spectra were found to remain constant and appearance potentials were reproducible to within the quoted error limits (one standard deviation) for independent runs.

RESULTS AND DISCUSSION

Mass spectra

The 70 eV mass spectra of dimethylzinc, trimethylaluminum, and trimethylantimony are listed in Table 1. To the best of the authors' knowledge, these mass spectra have not been reported previously.

TABLE 1

RELATIVE ABUNDANCES (AT 70 eV) OF THE PRINCIPAL POSITIVE IONS FORMED FROM DIMETHYLZINC, TRIMETHYLALUMINUM AND TRIMETHYLANTIMONY

Ion	Relative abundances		
	Zn(CH ₃) ₂	Al(CH ₃) ₃	Sb(CH ₃) ₃
M(CH ₃) ₃ ⁺		4.9	78.4
M(CH ₃) ₂ ⁺	36.6	100.0	100.0
M(CH ₂) ₂ ⁺			25.0
HM(CH ₃) ⁺	7.6	3.4	6.7
M(CH ₃) ⁺	100.0	6.3	35.6
M(CH ₂) ⁺	9.0	1.0	26.7
M(CH) ⁺	2.8		8.8
MC ⁺	1.3		
MH ₂ ⁺		2.3	7.2
MH ⁺	2.3	^a	12.6
M ⁺	16.6	36.5	36.7
CH ₃ ⁺	21.4	21.3	^b
M ₂ (CH ₃) ₅ ⁺		0.2	

^a Background due to air leak in the mass spectrometer. ^b Background due to n-heptane solvent.

The mass spectrum of dimethylzinc is similar to that of the dimethylmercury⁴. The dominant species is formed by removal of a CH₃ group from the parent molecule. Ions corresponding to the loss of hydrogen atoms from Zn(CH₃)⁺ ion also were

detected. The metal hydride ion ZnH^+ and the methyl metal hydride ion $\text{HZn}(\text{CH}_3)^+$ could only be formed by rearrangement mechanisms. The appearance of similar ions was not reported in Hobrock's cracking pattern of dimethylmercury¹⁷; however, Hobrock predicted such ions in the lighter members of the group IIB dimethyl compounds. Dibeler *et al.*¹⁻³ were the first to note this common formation of metal hydride ions in the mass spectra of metal alkyls.

The trimethylaluminum mass spectrum indicates association in the gas phase. The dimeric species $\text{Al}_2(\text{CH}_3)_5^+$ was detected in extremely low abundance. One might anticipate several dimeric ions of this type in the mass spectrum of this compound since it is known to be dimeric in the gaseous state¹⁸. However, only the dialuminum-pentamethyl ion was found in this study. Porter and Zeller¹⁹ noted the presence of Al_2F_5^+ of low intensity in the mass spectrum of aluminum fluoride; other similarities between these two dimetallic compounds exist. The most abundant metal-containing species we observed were Al^+ , AlCH_3^+ , $\text{Al}(\text{CH}_3)_2^+$, and $\text{Al}(\text{CH}_3)_3^+$; the analogous aluminum-fluorine ions were noted with similar intensities in the mass spectrum of aluminum fluoride¹⁹. Small abundances of the rearrangement ions AlH_2^+ and $\text{HAl}(\text{CH}_3)^+$ also were detected. Since N_2^+ (background in the mass spectrometer)

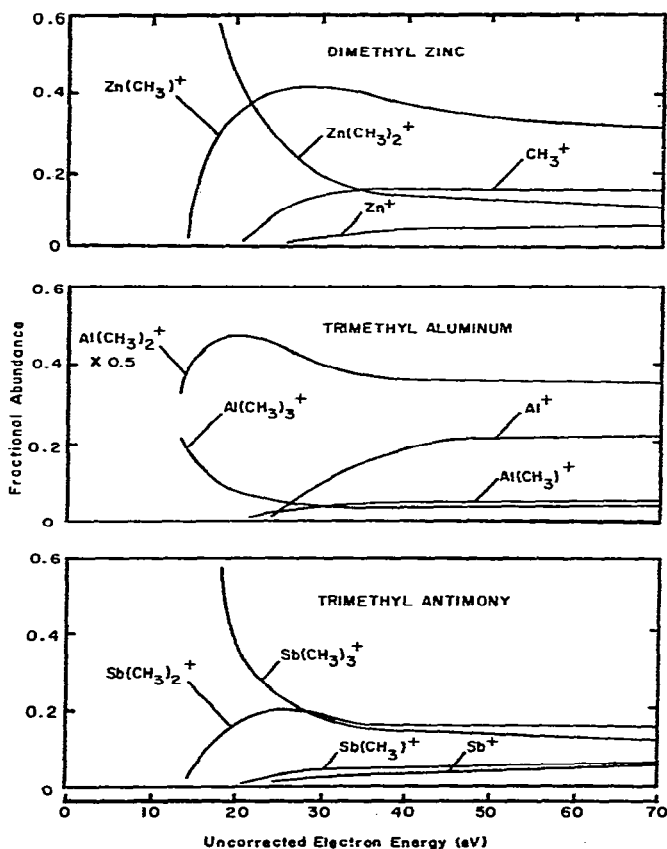


Fig. 1. Clastograms for Dimethylzinc, Trimethylaluminum, and Trimethylantimony.

occurs at the same m/e value as AlH^+ , studies of this ion (if, indeed, it exists) were not possible.

The mass spectrum of trimethylantimony is quite similar to the mass spectrum of trimethylphosphine¹⁰. Several ions are formed by loss of hydrogen atoms from the $Sb(CH_3)_x^+$ ions. The major ion was found to be the dimethylantimony ion; however, the parent molecule-ion is present here in high abundance. Antimony monohydride and dihydride ions were detected in addition to Sb^+ . The hydrocarbon fragment ions that may be formed from trimethylantimony could not be studied due to the production of similar ions¹⁶ from the solvent, *n*-heptane.

Clastograms and probable processes.

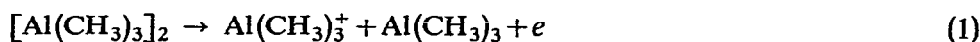
The clastograms for $Zn(CH_3)_2$, $Al(CH_3)_3$ and $Sb(CH_3)_3$ are shown in Fig. 1. The dependence of the fractional intensities of the fragment ions as a function of the ionizing energy is represented by such a figure. Between 35 and 70 eV there is little change in the fractional abundance of the ions. The dominant $ZnCH_3^+$, $Al(CH_3)_2^+$, and $Sb(CH_3)_2^+$ ions decrease in abundance at low voltages while the parent molecule ions increase in abundance. The shapes of the (parent minus methyl)⁺ ions indicate their participation as intermediates in consecutive unimolecular decompositions of these materials when subjected to electron bombardment.

For this reason it is believed that $M(CH_3)_x^+ \rightarrow M(CH_3)_{x-1}^+ + CH_3$ and further that $M(CH_3)_{x-1}^+ \rightarrow M(CH_3)_{x-2}^+ + CH_3$, and this is supported by the energetic considerations discussed below. Further, in the mass spectrum of $Pb(C_2H_5)_4$ metastable peaks corresponding to $Pb(C_2H_5)_3^+ \rightarrow Pb(C_2H_5)_2^+ + C_2H_5$ and $Pb(C_2H_5)_2^+ \rightarrow Pb(C_2H_5)^+ + C_2H_5$ have been observed¹⁻³. Although Carrick and Glockling²⁰ have identified alkene and H_2 eliminations by means of metastable peaks in the spectra of isopropylgermane and hexaisopropyldigermane, the loss of the CH_2 species from the metal methyl compounds is certainly not as favorable energetically. Thus, from the interpretation of the clastogram data, the above reasons, and the energetic data below, simple bond cleavages have been preferred in the probable processes written.

Ionization potentials

The ionization potentials determined for dimethylzinc, trimethylaluminum, and trimethylantimony are $8.8_6 \pm 0.1_5$, $9.0_9 \pm 0.2_6$, and $8.0_4 \pm 0.1_6$ eV, respectively. Reese and Dibeler have found $I[Zn(CH_3)_2]$ to be 9.09 ± 0.2 eV²¹.

One should note, however, that if the threshold energy measured for the formation of $Al(CH_3)_3^+$ ion is for its formation by ionization and subsequent dissociation of the dimer $[Al(CH_3)_3]_2$, *i.e.*,



the ionization potential of $Al(CH_3)_3$ would be 8.21 eV, according to the relation

$$I[Al(CH_3)_3] = A.P.[Al(CH_3)_3^+] - D[(CH_3)_3Al-Al(CH_3)_3] \quad (2)$$

where $A.P.[Al(CH_3)_3^+] = 9.09$ eV and $D[(CH_3)_3Al-Al(CH_3)_3] = 20.2$ kcal/mole²².

The ionization potentials of the methyl-substituted metal compounds of groups IIB, IIIA, IVA, and VA are summarized in Table 2. Several trends are noted in the ionization potentials of these molecules. By utilizing these trends, the ionization potentials of unstudied $M(CH_3)_x$ molecules have been estimated.

TABLE 2

COMPARISON OF IONIZATION POTENTIALS (IN eV) OF $M(\text{CH}_3)_x$ MOLECULES

Group IIB	Group IIIA	Group IVA	Group VA
	$\text{B}(\text{CH}_3)_3$	$\text{C}(\text{CH}_3)_4$	$\text{N}(\text{CH}_3)_3$
	8.8 (ref. 6)	10.37 (ref. 23)	7.82 (ref. 9)
	$\text{Al}(\text{CH}_3)_3$	$\text{Si}(\text{CH}_3)_4$	$\text{P}(\text{CH}_3)_3$
	9.09	9.8 (ref. 4)	8.60 (ref. 10)
$\text{Zn}(\text{CH}_3)_2$	$\text{Ga}(\text{CH}_3)_3$	$\text{Ge}(\text{CH}_3)_4$	$\text{As}(\text{CH}_3)_3$
8.86	(8.8) ^a	9.2 (ref. 4)	8.3 (ref. 11)
$\text{Cd}(\text{CH}_3)_2$	$\text{In}(\text{CH}_3)_3$	$\text{Sn}(\text{CH}_3)_4$	$\text{Sb}(\text{CH}_3)_3$
(8.9) ^a	(8.5) ^a	8.25 (ref. 4)	8.04
$\text{Hg}(\text{CH}_3)_2$	$\text{Tl}(\text{CH}_3)_3$	$\text{Pb}(\text{CH}_3)_4$	$\text{Bi}(\text{CH}_3)_3$
8.90 (ref. 4)	(8.2) ^a	8.0 (ref. 4)	(7.8) ^a

^a Estimated values.

The ionization potentials of the group IIB compounds, $\text{Zn}(\text{CH}_3)_2$ and $\text{Hg}(\text{CH}_3)_2$ are 8.86 ± 0.15 and 8.90 ± 0.20 eV, respectively. The ionization potential of the remaining member of this series, $\text{Cd}(\text{CH}_3)_2$, is predicted to be ~ 8.9 eV.

Removal of an electron from the group A compounds in Table 2 becomes more difficult, in general, as the atomic number of the central metal atom decreases within a given family. Exceptions to this general trend are: $I[\text{N}(\text{CH}_3)_3] < I[\text{P}(\text{CH}_3)_3]$, and $I[\text{B}(\text{CH}_3)_3] < I[\text{Al}(\text{CH}_3)_3]$. Ionization becomes easier as the central atom becomes more metallic. Ionization becomes more difficult for methyl compounds of the more electronegative elements. This is illustrated by the high ionization potentials of the monohalomethanes²³. The exceptions to this trend are the group VA compounds.

By considering the above observations in the ionization potential data determined in this study and the data available in the literature, the following ionization potentials are estimated for the remaining A group compounds: group IIIA: $I[\text{Ga}(\text{CH}_3)_3] \approx 8.8$ eV, $I[\text{In}(\text{CH}_3)_3] \approx 8.5$ eV, and $I[\text{Tl}(\text{CH}_3)_3] \approx 8.2$ eV; and group VA: $I[\text{Bi}(\text{CH}_3)_3] \approx 7.8$ eV.

Dimethylzinc appearance potentials

Calculations of the heats of formation for the ions produced from dimethylzinc were made using a value of 13.3 kcal/mole for the heat of formation of dimethylzinc²⁴.

The ΔH_f of ZnCH_3^+ was calculated to be 241 kcal/mole. The bond dissociation energies, $D[(\text{CH}_3)\text{-Zn}(\text{CH}_3)] = 47$ and $D(\text{Zn-CH}_3) = 35$ kcal/mole, are given by Cottrell²⁵. These data allow the ionization potential of the ZnCH_3 radical to be calculated using the relation

$$I(\text{ZnCH}_3) = \Delta H_f(\text{ZnCH}_3^+) - D(\text{CH}_3\text{-ZnCH}_3) + \Delta H_f(\text{CH}_3) - \Delta H_f[\text{Zn}(\text{CH}_3)_2] \quad (3)$$

Such a calculation yields an ionization potential of 9.2 eV for ZnCH_3 .

From the appearance potential of CH_3^+ ion one may deduce that the accompanying neutral fragment is not the ZnCH_3 radical. The neutral fragments proposed are $\text{CH}_3 + \text{Zn}$. A heat of formation of CH_3^+ (298 kcal/mole) is calculated. Although this value is greater than the established value of 262 kcal/mole²⁶, due to excess

energy involved in the reaction, the proposed process best satisfies the energetics.

On the basis of the comparison of the literature value for the heat of formation of Zn^+ (249 kcal/mole)²⁷ with $\Delta H_f(Zn^+)$ (258 kcal/mole), calculated for the accompanying formation of two neutral methyl fragments, it is believed that the process of formation of the Zn^+ ion from dimethylzinc is that shown in Table 3. The energetics rule out the formation of ethane in the threshold region.

TABLE 3

APPEARANCE POTENTIALS AND HEATS OF FORMATION OF THE PRINCIPAL POSITIVE IONS PRODUCED FROM DIMETHYLZINC

Ion	Appearance potential (eV)	Probable process	$\Delta H_f(\text{ion})$ (kcal/mole)
$Zn(CH_3)_2^+$	$8.8_6 \pm 0.1_5$	$Zn(CH_3)_2 \rightarrow Zn(CH_3)_2^+$	218
$ZnCH_3^+$	11.2 ± 0.2	$\rightarrow ZnCH_3^+ + CH_3$	241
ZnH^+	13.9 ± 0.4	$\rightarrow ZnH^+ + CH_3 + CH_2$	233
Zn^+	13.4 ± 0.3	$\rightarrow Zn^+ + 2 CH_3$	258
CH_3^+	15.1 ± 0.5	$\rightarrow CH_3^+ + CH_3 + Zn$	298

Trimethylaluminum appearance potentials

Long and Norrish²⁴ have reported the heat of formation of gaseous monomeric $Al(CH_3)_3$ to be -13.3 kcal/mole. This value was employed in the calculations of the heats of formation of the gaseous ions shown in Table 4.

TABLE 4

APPEARANCE POTENTIALS AND HEATS OF FORMATION OF THE PRINCIPAL POSITIVE IONS PRODUCED FROM TRIMETHYLALUMINUM^a

Ion	Appearance potential (eV)	Probable process	$\Delta H_f(\text{ion})$ (kcal/mole)
$Al(CH_3)_3^+$	$9.0_9 \pm 0.2_6$	$Al(CH_3)_3 \rightarrow Al(CH_3)_3^+$	196
$Al(CH_3)_2^+$	10.1 ± 0.3	$\rightarrow Al(CH_3)_2^+ + CH_3$	188
$AlCH_3^+$	13.9 ± 0.3	$\rightarrow AlCH_3^+ + 2 CH_3$	243
Al^+	14.6 ± 0.2	$\rightarrow Al^+ + 3 CH_3$	227

^a If the parent-molecule is the dimeric species, $Al_2(CH_3)_6$, all $\Delta H_f(\text{ion})$ values will be 20 kcal/mole lower, and $Al(CH_3)_3$ would be the additional product in the probable processes listed.

The heats of formation for $Al(CH_3)_2^+$ and $AlCH_3^+$ were calculated to be 188 and 243 kcal/mole, respectively. The average $Al-(CH_3)$ bond energy in trimethylaluminum has been reported²⁵ to be 61 kcal/mole. In light of the values of $D(CH_3Zn-CH_3)$, $D(CH_3-Zn)$ and $E(Zn-CH_3)$ given by Cottrell²⁵ and the values of $D[(CH_3)_3-Sn-CH_3]$ and $E(Sn-CH_3)$ given by Yergey and Lampe²⁸ and Lippincott and Tobin²⁹, respectively, we estimate $D[(CH_3)_2Al-CH_3] = 80$ and $D(CH_3Al-CH_3) = 61$ kcal/mole. Then, by using a thermochemical approach similar to that discussed previously for $Zn(CH_3)$ (eqn. 3), the ionization potentials of $Al(CH_3)_2$ and $AlCH_3$ are estimated to be 6.6 and 7.8 eV, respectively.

The process chosen for the formation of Al^+ is elimination of three neutral methyl fragments, analogous to the process chosen for the formation of M^+ in

other metal alkyls. The calculated heat of formation of $\text{Al}^+ = 227$ kcal/mole is in reasonably good agreement with 216 kcal/mole reported in the literature²⁷. If, however, one were to consider the Al^+ ion being formed from the dimer $\text{Al}_2(\text{CH}_3)_6$ by fragmenting three methyl groups and $\text{Al}(\text{CH}_3)_3$, $\Delta H_f(\text{Al}^+) = 207$ kcal/mole. Since the appearance potential is generally considered an upper limit for a fragmentation process, it is postulated that the process occurring at the threshold is ionization and subsequent dissociation of the monomeric $\text{Al}(\text{CH}_3)_3$ species.

Trimethylantimony appearance potentials

The heat of formation of gaseous trimethylantimony has been reported by Long and Sackman³⁰ to be 6.4 kcal/mole. This value was used in the thermochemical calculations of the heats of formation of the gaseous ions listed in Table 5.

TABLE 5

APPEARANCE POTENTIALS AND HEATS OF FORMATION OF THE PRINCIPAL POSITIVE IONS PRODUCED FROM TRIMETHYLANTIMONY

Ion	Appearance potential (eV)	Probable process	$\Delta H_f(\text{ion})$ (kcal/mole)
$\text{Sb}(\text{CH}_3)_3^+$	$8.0_4 \pm 0.1_6$	$\text{Sb}(\text{CH}_3)_3 \rightarrow \text{Sb}(\text{CH}_3)_3^+$	192
$\text{Sb}(\text{CH}_3)_2^+$	10.5 ± 0.2	$\rightarrow \text{Sb}(\text{CH}_3)_2^+ + \text{CH}_3$	217
$\text{Sb}(\text{CH}_2)_2^+$	12.6 ± 0.3	$\rightarrow \text{Sb}(\text{CH}_2)_2^+ + \text{CH}_3 + \text{H}_2$	265
HSbCH_3^+	13.4 ± 0.3	$\rightarrow \text{HSb}(\text{CH}_3)^+ + \text{CH}_3 + \text{CH}_2$	215
SbCH_3^+	14.3 ± 0.2	$\rightarrow \text{SbCH}_3^+ + 2 \text{CH}_3$	272
SbCH_2^+	15.1 ± 0.2	$\rightarrow \text{SbCH}_2^+ + 2 \text{CH}_3 + \text{H}$	239
SbCH^+	13.7 ± 0.4	$\rightarrow \text{SbCH}^+ + 2 \text{CH}_3 + \text{H}_2$	258
SbH_2^+	13.7 ± 0.2	$\rightarrow \text{SbH}_2^+ + \text{CH}_3 + 2 \text{CH}_2$	154
SbH^+	14.5 ± 0.5	$\rightarrow \text{SbH}^+ + 2 \text{CH}_3 + \text{CH}_2$	209
Sb^+	14.8 ± 0.4	$\rightarrow \text{Sb}^+ + 3 \text{CH}_3$	252

The heat of formation of Sb^+ (252 kcal/mole), calculated on the basis of the process chosen in Table 5, is in good agreement with the reported spectroscopic value of 260 kcal/mole²⁷. Therefore, the process chosen for the formation of Sb^+ involving the elimination of neutral CH_3 groups further substantiates this type of process in the methyl-substituted group-A metal compounds.

Similar processes involving loss of methyl groups are postulated for the $\text{Sb}(\text{CH}_3)_x^+$ type ions where $x = 1$ and 2. The calculated heats of formation of 265 and 272 kcal/mole for $\text{Sb}(\text{CH}_3)_2^+$ and SbCH_3^+ ions, respectively, and an average value for the $\text{Sb}-\text{CH}_3$ bond energy of 47 kcal/mole²⁵ have been used together with the estimated $D[(\text{CH}_3)_2\text{Sb}-\text{CH}_3] = 65$ and $D(\text{CH}_3\text{Sb}-\text{CH}_3) = 47$ kcal/mole, arrived at in a manner similar to that in the $\text{Al}(\text{CH}_3)_3$ treatment above, to estimate the ionization potentials of the analogous dimethyl and monomethyl radicals; the results are $I[\text{Sb}(\text{CH}_3)_2] = \approx 7.7$ eV and $I(\text{SbCH}_3) \approx 9.4$ eV.

The appearance potentials for SbCH_2^+ and SbCH^+ are 15.1 and 13.7 eV, respectively. The lower appearance potential of the SbCH^+ ion suggests a greater stability in the accompanying neutral species. This is shown in Table 5 in the process for the formation of the SbCH^+ ion. The H_2 molecule tends to lower the appearance potential of SbCH^+ below that of SbCH_2^+ where H is fragmented from the molecule.

The various other fragment ions formed by unimolecular decomposition are

presented in Table 5 together with the calculated heats of formation and the probable processes that are consistent with the energetics.

SUMMARY

Ionization and appearance potentials determined with a time-of-flight mass spectrometer are reported for the principal positive ions in the mass spectra of dimethylzinc, trimethylaluminum, and trimethylantimony. The heats of formation, deduced by the application of the experimentally determined energetics and additional thermochemical data, have been listed for the principal positive ions of the three metal alkyls. The observed ionization potentials for $\text{Zn}(\text{CH}_3)_2$ ($8.8_6 \pm 0.1_5$ eV), $\text{Al}(\text{CH}_3)_3$ ($9.0_9 \pm 0.2_6$ eV), and $\text{Sb}(\text{CH}_3)_3$ ($8.0_4 \pm 0.1_6$ eV) are compared to the ionization potentials reported previously for methyl-substituted metal compounds. Additionally, the ionization potentials of the following radicals have been estimated: $\text{Zn}(\text{CH}_3) \approx 9.2$ eV; $\text{Al}(\text{CH}_3)_2 \approx 6.6$ eV; $\text{AlCH}_3 \approx 7.8$ eV; $\text{Sb}(\text{CH}_3)_2 \approx 7.7$ eV; and $\text{SbCH}_3 \approx 9.4$ eV.

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