

AN ELECTRON IMPACT STUDY OF IONIZATION AND DISSOCIATION OF TRIMETHYLSTANNANES

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SUMMARY

Appearance potentials of ions from a series of trimethylstannanes were measured. Combination of these data with molecular and radical heats of formation, with the assumption of zero excess energy on electron impact ionization, yields a value of $\Delta H_f[(\text{CH}_3)_3\text{Sn}] = 32 \pm 6$. Also from these data an ionization potential of the trimethylstannyl radical of 6.8 ± 0.3 eV is derived, in good agreement with direct measurement. The dissociation energies of the $(\text{CH}_3)_3\text{Sn-X}$ bonds are shown to be about 10–12 kcal·mole⁻¹ lower than in the corresponding $(\text{CH}_3)_3\text{C-X}$ bonds. value of $\Delta H_f[(\text{CH}_3)_3\text{Sn}] = 32 \pm 6$. Also from these data an ionization potential of the

A considerable fraction of the available data on bond dissociation energies, molecular ionization potentials, and free radical ionization potentials has come from studies of the behavior of molecules subjected to electron impact¹⁻⁵. Such knowledge has proven to be of interest and importance in questions of electronic structure and of rates and mechanisms of chemical reactions. However, most of this large body of energetic data pertains to molecules, radicals, and ions that are generally thought of as belonging to the realm of organic chemistry. In the rapidly growing field of organometallic chemistry very little such energetic data is available for guidance in structural, mechanistic and rate considerations. Indeed, in many areas of organometallic chemistry not even the standard heats of formation of the stable compounds are known.

In the case of organotin compounds, however, a body of thermochemical data is available⁶⁻¹³ (although some of the older work, as recently pointed out¹³, is unreliable) and makes feasible electron impact studies directed toward the determination of the energetic properties of the organotin molecule, ions, and free radicals. In this paper we describe a study on the ionization and dissociation of some trimethyltin derivatives by electron impact. Some preliminary results of this study were published previously^{14,15}.

EXPERIMENTAL

The appearance potentials of the $(\text{CH}_3)_3\text{Sn}^+$ and $(\text{CH}_3)_2\text{SnX}^+$ ions were determined using the retarding-potential-difference (RPD) method¹⁶ in either a Bendix Model 14-101 time-of-flight mass spectrometer^{17,18} or a Nuclide Associates Model 12-90G magnetic sector mass spectrometer. In both instruments the difference ion-currents were obtained for 0.1 volt changes in the retarding potential. The actual

potential applied to the retarding grid in the electron gun was usually of the order of 0.2 to 0.5 volts negative with respect to the filament, the actual value being obtained empirically at the start of an experiment as that potential which resulted in the largest change of ion-current for a 0.1 volt change in retarding potential. The appearance potentials of the $(\text{CH}_3)_3\text{Sn}^+$ ion from $(\text{CH}_3)_4\text{Sn}$, $(\text{CH}_3)_3\text{SnC}_2\text{H}_5$ and $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ were measured with the RPD technique in both instruments and, in addition, with a monoenergetic electron beam (± 0.05 eV) as obtained from a 127° velocity selector¹⁹⁻²⁶. The selector was constructed for another purpose and was mounted within a Nuclide Associates 12-90G spectrometer. In all cases the ionizing electron beam current was less than $0.1 \mu\text{-amperes}$. The results obtained are shown in Table 1.

With the exception of the appearance potential of $(\text{CH}_3)_3\text{Sn}^+$ from $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ the results from the several ion sources are in excellent agreement. The agreement of the appearance potentials in the case of $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ are not in very good agreement, the total spread being 0.30 eV. However, it must be pointed out that only one determination was made with the velocity selector. Secondly, the average value from the two extreme values would be 9.80 ± 0.15 which compares favorably with the average value of 9.82 ± 0.15 obtained from 16 determinations using the RPD method in the time-of-flight instrument. Hence, we consider the values in Table 1 to be in satisfactory agreement.

In all compounds studied the intensities of the molecular ions, $(\text{CH}_3)_3\text{SnX}^+$, were very low, which precluded accurate ionization potential measurements using the RPD technique or the electron velocity selector. Instead, the ionization potentials of the molecules were determined from the ionization efficiency curves using the method of Lossing *et al.*²⁷.

Xenon was used in most cases as an internal standard to calibrate the electron energy scale, although in a few instances, where mass interference was suspected, CS_2 was employed. It was discovered early in this work that tungsten filaments had a very short life in the presence of organotin compounds. On the other hand rhenium filaments were quite satisfactory and were used throughout the course of the work.

Very pure samples ($>99.5\%$) of the trimethyltin compounds were kindly supplied by Dr. W. J. Considine of M & T Chemicals Co., Rahway, N. J. With the exception of degassing, these samples were used as received. Monoisotopic stannane ($^{120}\text{SnH}_4$) was prepared from 98.39% pure monoisotopic ^{120}Sn (obtained from Oak Ridge National Laboratory) using the method of Schaeffer and Emilius²⁸. Due to the instability of stannane, all measurements were made within 24 hours of preparation.

TABLE 1

COMPARISON OF THREE ION SOURCES

Numbers in parantheses indicate number of runs.

Ion source	Appearance potential of $(\text{CH}_3)_3\text{Sn}^+$ in eV		
	$(\text{CH}_3)_3\text{SnCH}_3$ (<i>m/e</i> 165)	$(\text{CH}_3)_3\text{Sn-Sn}(\text{CH}_3)_3$ (<i>m/e</i> 165)	$(\text{CH}_3)_3\text{SnC}_2\text{H}_5$ (<i>m/e</i> 165)
RPD-Bendix	$9.72 \pm 0.06(10)$	$9.82 \pm 0.15(16)$	$9.49 \pm 0.07(15)$
RPD-Nuclide	$9.74 \pm 0.03(2)$	$9.95 \pm 0.04(4)$	
EVS-Nuclide	$9.65 (1)$	$9.65 (1)$	$9.50 (1)$

RESULTS AND DISCUSSION

*Mass spectra**

The dominating feature of the mass spectra of the alkyltin compounds is the isotopic distribution of tin. When the observed spectra are corrected for this isotopic distribution it is seen that even at 70 eV the only significant bond rupture is of C-Sn and Sn-Sn bonds. For example, consider the ions of interest to us in the electron impact spectra of $(\text{CH}_3)_3\text{Sn-i-C}_3\text{H}_7$, namely the ions $(\text{CH}_3)_3\text{Sn}^+$, $(\text{CH}_3)_2\text{Sn-i-C}_3\text{H}_7^+$, and the parent ion $(\text{CH}_3)_3\text{Sn-i-C}_3\text{H}_7^+$. Assuming that no C-H bond rupture occurs we can calculate the distribution of masses for the various ions simply on the basis of the ^{13}C and Sn(112, 114, 115, 116, 117, 118, 119, 120, 121, 122, and 124) isotopic ratios. The agreement of the calculated and measured spectra, as shown in Fig. 1,

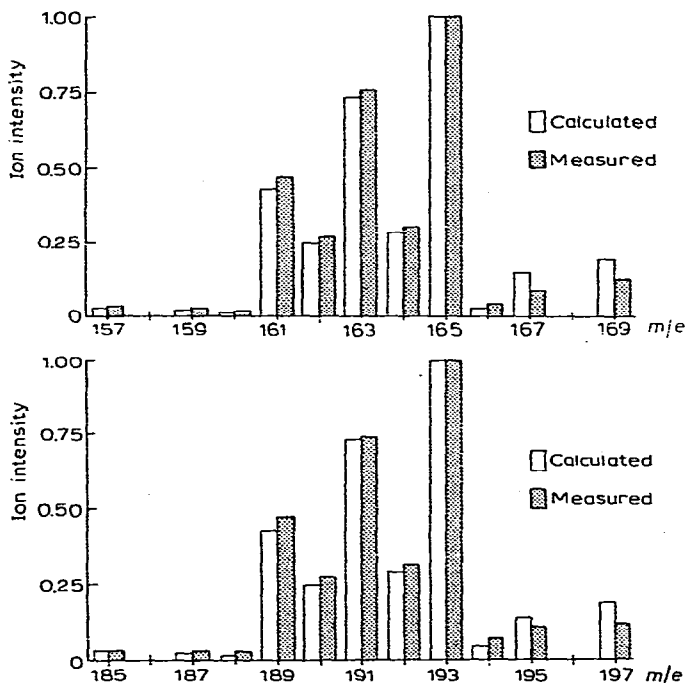
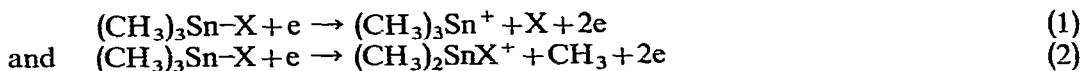


Fig. 1. Comparison of observed and calculated relative intensities of the $(\text{CH}_3)_3\text{Sn}^+$ and $(\text{CH}_3)_2\text{SnC}_3\text{H}_7^+$ ions in the mass spectrum of trimethyl-sec-propylstannane.

indicates that in our appearance potential measurements we are indeed measuring the energetics of the simple processes



free from any interference due to C-H bond rupture.

* Note added in proof. A recent paper by Boué, Gielen and Nasielski (*Bull. Soc. Chim. Belges*, 77 (1968) 43) reports 70 eV mass spectra of a number of $(\text{CH}_3)_3\text{Sn-R}$ compounds, where R includes CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, $(\text{CH}_3)_2\text{CH}$, $n\text{-C}_4\text{H}_9$ and $(\text{CH}_3)_3\text{C}$. In these cases, which are the only ones comparable with our work, the agreement of the mass spectra is quite good.

Appearance potentials

Table 2 gives all the ionization and appearance potentials measured, together with the average deviations of replicate measurements and, parenthetically, the number of determinations for each appearance potential. The reproducibility of most of the values is very good with only a few average deviations exceeding 0.15 eV. We were not able to obtain very precise data for the appearance potential of the

TABLE 2

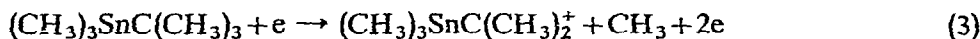
IONIZATION AND APPEARANCE POTENTIALS IN TRIMETHYLTIN COMPOUNDS
Numbers in parentheses indicate number of runs.

Molecule	I_z	Appearance potentials	
		$(\text{CH}_3)_3\text{Sn}^+$	$(\text{CH}_3)_2\text{SnX}^+$
$(\text{CH}_3)_4\text{Sn}$	$8.76 \pm 0.02(5)$	$9.72 \pm 0.03(13)$	—
$(\text{CH}_3)_3\text{Sn}-\text{C}_2\text{H}_5$		$9.49 \pm 0.07(15)$	$9.88 \pm 0.02(3)$
$(\text{CH}_3)_3\text{Sn}-\text{C}_2\text{H}_3$		$10.44 \pm 0.11(8)$	$9.56 \pm 0.08(12)$
$(\text{CH}_3)_3\text{Sn}-n-\text{C}_3\text{H}_7$	$8.54 \pm 0.01(5)$	$9.50 \pm 0.06(8)$	$9.59 \pm 0.07(5)$
$(\text{CH}_3)_3\text{Sn}-i-\text{C}_3\text{H}_7$	$8.28 \pm 0.01(5)$	$9.17 \pm 0.14(9)$	$10.03 \pm 0.04(6)$
$(\text{CH}_3)_3\text{Sn}-\text{C}_3\text{H}_5$		$8.68 \pm 0.02(3)$	$9.43 \pm 0.20(3)$
$(\text{CH}_3)_3\text{Sn}-n-\text{C}_4\text{H}_9$		$9.80 \pm 0.04(3)$	$9.67 \pm 0.09(7)$
$(\text{CH}_3)_3\text{Sn}-\text{sec}-\text{C}_4\text{H}_9$	$8.27 \pm 0.01(5)$	$9.20 \pm 0.05(3)$	$9.76 \pm 0.19(3)$
$(\text{CH}_3)_3\text{Sn}-i-\text{C}_4\text{H}_9$	$8.34 \pm 0.02(5)$	$9.79 \pm 0.12(3)$	$9.62 \pm 0.02(3)$
$(\text{CH}_3)_3\text{Sn}-t-\text{C}_4\text{H}_9$		$9.50 \pm 0.10(7)$	$10.95 \pm 0.19(4)^c$
$(\text{CH}_3)_3\text{Sn}-\text{Sn}(\text{CH}_3)_3$	$8.08 \pm 0.02(5)$	$9.85 \pm 0.16(21)$	$8.17 \pm 0.03(3)^a$
$^{120}\text{SnH}_4$		$11.31 \pm 0.01(5)^b$	—

^a $(\text{CH}_3)_2\text{Sn}-\text{Sn}(\text{CH}_3)_3^+$. ^b H_3Sn^+ . ^c Probably represents formation of $(\text{CH}_3)_3\text{SnC}(\text{CH}_3)_3^+$.

$(\text{CH}_3)_3\text{Sn}^+$ ion from hexamethyldistannane because of the very low vapor pressure of this material. For this reason many determinations, (21), of this quantity were carried out over a long period of time, the result being an average value of 9.85 eV with an average deviation of 0.16 eV and with a maximum spread in the measurements of 0.56 eV.

The average value of four determinations of the appearance potential of the m/e 207 ion from trimethyl-tert-butylstannane, namely 10.95 eV, seems to be inordinately high, even within the rather large average deviation, when compared to the appearance potentials of the other $(\text{CH}_3)_2\text{SnY}^+$ ions. It is to be noted that the appearance potential found for this ion lies close to the values found for the appearance potentials of ions formed as a result of loss of CH_3 from the $(\text{CH}_3)_3\text{C}$ group^{29,30}. For example, $A[(\text{CH}_3)_3\text{C}^+]$ from $(\text{CH}_3)_4\text{C}$ is 10.83 eV²⁹ and $A[(\text{CH}_3)_2\text{CCl}^+]$ from $(\text{CH}_3)_3\text{CCl}$ is 10.77 eV³⁰. Thus we think that the only reasonable rationalization of the high value found for m/e 207 from trimethyl-tert-butylstannane is that it refers to the energy change of reaction (3), viz.:



which must then be more probable than the energetically lower reaction (4). In support of this point of view three of the four ionization efficiency curves of m/e 207 showed



evidence of a very low intensity tail towards lower energies. However, again vapor pressure limitations of this compound made a separation of these two processes and a precise extrapolation of this low intensity tail impossible. Thus the value of 10.95 reported is probably an average of the onset potentials of processes (3) and (4) that is weighted very heavily in favor of (3). If any meaning is to be ascribed to this value it should be that it lies close to the appearance potential of (3) (being most likely a lower limit).

In the case of the molecular ionization potentials we were able to obtain meaningful data only on those shown in Table 2. The intensities of the molecular ions were quite small and hence the values of the onset potentials for these ions are quite subject to the influence of impurities. We made such measurements only when the distribution of intensities at the parent mass matched the isotopic distribution of Sn.

There are very few appearance potentials reported in the literature with which we may compare our results. Hobrock and Kiser³¹ and Occolowitz³² report the appearance potential of $(\text{CH}_3)_3\text{Sn}^+$ from $(\text{CH}_3)_3\text{Sn}$ to be 9.9 ± 0.15 eV and 9.7 ± 0.2 eV, respectively, in satisfactory agreement with our results. Hobrock and Kiser³¹ also report the ionization potential of $(\text{CH}_3)_4\text{Sn}$ to be 8.25 ± 0.15 as compared with our value of 8.76 ± 0.02 eV. We have no explanation for this disagreement, which lies outside of the experimental error, but in view of the concordance of our value with the ionization potentials of the other organotin compounds, we see no reason to mistrust it. Saalfeld and Svec³³ reported an appearance potential of 9.9 ± 0.15 eV for SnH_3^+ from SnH_4 which is considerably lower than our value of 11.31 ± 0.01 . In an earlier publication, however, these same authors report an appearance potential of 11.9 ± 0.2 eV for SnH_3^+ from SnH_4 ³⁴. They give no explanation in their later paper for this discrepancy and since our value falls between these extremes we tend to think it more nearly correct.

Bond dissociation energies

In order to calculate energetic quantities of interest in trimethylstannanes from

TABLE 3

MOLECULAR, RADICAL AND IONIC HEATS OF FORMATION IN $(\text{CH}_3)_3\text{SnX}$ COMPOUNDS

X	$\Delta H_f[(\text{CH}_3)_3\text{SnX}]$ (kcal·mole ⁻¹)		$\Delta H_f(\text{X})$ (kcal·mole ⁻¹)	Reference	$\Delta H_f[(\text{CH}_3)_3\text{Sn}^+]$ (kcal·mole ⁻¹)
	Found	Calcd.			
CH_3	-4.6 ± 0.6		32 ± 1	3	187
C_2H_5	-7.1 ± 0.7	- 6.55	25 ± 2	3	188
$\text{CH}_3\text{CH}_2\text{CH}_2$		-11.58	22 ± 3	3	186
$(\text{CH}_3)_2\text{CH}$	-11.2 ± 1.1	-10.98	17 ± 2	3	183
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$		-16.51	16 ± 2	46	194
$(\text{CH}_3)_2\text{CHCH}_2$		-18.54	14 ± 2	46	193
$\text{CH}_3\text{CH}_2\text{CH}-\text{CH}_3$		-15.91	12 ± 2	46	184
$(\text{CH}_3)_3\text{C}$	-16.0 ± 1.8	-17.04	7 ± 2	47	195
$\text{CH}_2=\text{CH}$	$+22.1 \pm 1.3$		65 ± 3	3	198
$(\text{CH}_3)_3\text{Sn}$	-5.4 ± 2.3		32 ± 6	a	

^a Calculated in this work. See text.

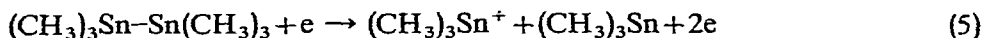
the data in Table 2, the standard heats of formation of the parent molecules as well as of the free radicals, X, produced in (1) are required. With regard to the molecular heats of formation, Skinner and coworkers have determined experimentally the standard heats of formation of $(\text{CH}_3)_4\text{Sn}^{12}$, $(\text{CH}_3)_3\text{SnC}_2\text{H}_5^{12}$, $(\text{CH}_3)_3\text{SnCH}=\text{CH}_2^{12}$, $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3^{12}$, $(\text{CH}_3)_3\text{SnC}(\text{CH}_3)_3^{13}$ and $(\text{CH}_3)_3\text{SnCH}(\text{CH}_3)_2^{13}$. Moreover, Coleman and Skinner¹³ have shown that the bond-energy and bond-interaction scheme of Allen^{35,36} works reasonably well when applied to the calculation of the standard heats of formation of tetraalkyltin compounds. In Table 3 we present the heats of formation of the pertinent compounds as measured by Skinner *et al.*^{12,13} and calculated using the data of Coleman and Skinner¹³ and the Allen bond-energy and bond-interaction scheme. In the last column of Table 3, we list the standard heats of formation of the $(\text{CH}_3)_3\text{Sn}^+$ as calculated from the thermochemical data and the appearance potentials of this ion shown in Table 2. In making the calculation of $\Delta H_f[(\text{CH}_3)_3\text{Sn}^+]$ we have assumed that there is no excess energy involved in the dissociative ionization, (1), so that, within the validity of this assumption, the appearance potential represents the enthalpy change of the reaction. Considering the uncertainties involved in the accuracy of the appearance potentials ($\approx \pm 0.1$ eV) and in the thermochemical data, the "constancy" of $\Delta H_f[(\text{CH}_3)_3\text{Sn}^+]$ is satisfactory. These

TABLE 4

BOND DISSOCIATION ENERGIES IN TRIMETHYLSTANNANES

X	$D[(\text{CH}_3)_3\text{Sn-X}]$ (kcal·mole ⁻¹)	$\bar{E}[(\text{CH}_3)_3\text{Sn-X}]$ (kcal·mole ⁻¹)	$D[(\text{CH}_3)_3\text{C-X}]$ (kcal·mole ⁻¹)
CH ₃	69 ± 6	51	79 ± 2
CH ₃ CH ₂	64 ± 6	47	76 ± 3
CH ₃ CH ₂ CH ₂	66 ± 7	49	78 ± 3
CH ₃ CH ₂ CH ₂ CH ₂	65 ± 6	48	77 ± 3
(CH ₃) ₂ CH CH ₂	65 ± 6	48	75 ± 3
(CH ₃) ₂ CH	60 ± 6	43	73 ± 3
CH ₃ CH ₂ (CH ₃)CH	60 ± 6	43	72 ± 3
(CH ₃) ₃ C	55 ± 6	38	68 ± 3
CH ₂	75 ± 7	58	86 ± 3
C ₆ H ₅	78 ± 6	61	87 ± 4
C ₆ H ₅ CH ₂	78 ± 6	61	87 ± 4
C ₆ H ₅ CH ₂	54 ± 6	37	61 ± 4
Br	91 ± 6	74	62 ± 4
I	77 ± 6	59	47 ± 4
(CH ₃) ₃ Sn	69 ± 8	35	

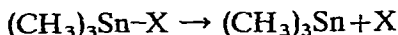
data yield an average value for this quantity of $\Delta H_f[(\text{CH}_3)_3\text{Sn}^+] = 190$ kcal·mole⁻¹, with a probable error of ± 4 kcal·mole⁻¹. With this value of $\Delta H_f[(\text{CH}_3)_3\text{Sn}^+]$, we again invoke, as an approximation, the assumption of zero excess energy in the process



to calculate the heat of formation of the $(\text{CH}_3)_3\text{Sn}$ radical. The value obtained is $\Delta H_f[(\text{CH}_3)_3\text{Sn}] = 32 \pm 6$ kcal·mole⁻¹ and is given in the 4th column of Table 3.

Given now a value for the heat of formation of the trimethylstannyl radical,

we may calculate the bond dissociation energy for any bond, $(\text{CH}_3)_3\text{Sn-X}$, for which the standard heats of formation of the molecule and the radical X are known. Of course, to equate the bond dissociation energy $D[(\text{CH}_3)_3\text{Sn-X}]$ to the enthalpy change of the reaction

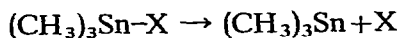


requires that the activation energy for the combination of the radicals, $(\text{CH}_3)_3\text{Sn}$ and X , be zero. Within our large uncertainty of $\pm 6 \text{ kcal}\cdot\text{mole}^{-1}$, this is most likely true. The bond dissociation energies so calculated for a number of molecules whose heats of formation have been measured^{12,13} or calculated by the Allen scheme^{35,36} are given in the second column of Table 4. In the third column of Table 4 we list the average thermochemical bond energies, designated \bar{E} , which are computed from the molecular and radical heats of formation in the usual way¹². Additional free radical heats of formation used to calculate the bond dissociation energies in Table 4 are as follows: $\Delta H_f(\text{C}_6\text{H}_5) = 72 \pm 2^{37}$; $\Delta H_f(\text{C}_6\text{H}_5\text{CH}_2) = 42 \pm 3^{38}$; $\Delta H_f(\text{Sn}) = 72^{39\text{a,b}}$, all in $\text{kcal}\cdot\text{mole}^{-1}$.

Also shown in the last column of Table 4 are the bond dissociation energies for the corresponding compounds in which the tin atom has been replaced by a carbon atom. The dissociation energies in the hydrocarbons were calculated from the molecular heats of formation³⁹ and the free radical heats of formation in Table 3. In a few instances it was necessary to estimate the molecular heat of formation and this was down using the method of Franklin⁴⁰.

It is seen that with the exception of the bromo and iodo derivatives the C-X bond is stronger than the Sn-X bond by about 10–13 $\text{kcal}\cdot\text{mole}^{-1}$. The bonding of the Sn to the halogens is on the other hand, some 30 $\text{kcal}\cdot\text{mole}^{-1}$ stronger than is the corresponding carbon-halogen bond. This is probably a reflection of strong $\text{Sn}^+ - \text{X}^-$ contributions to the bond strength that are a result of the low ionization potential of Sn and the high electron affinity of the halogen atom. The effect on the bond dissociation energy of the structure of the alkyl leaving-group is seen to follow the same trend as for hydrocarbons. Thus, we see that when RCH_2- is bonded to $(\text{CH}_3)_3\text{M}$ we have a dissociation energy of 64–66 $\text{kcal}\cdot\text{mole}^{-1}$ for $\text{M}=\text{Sn}$ and of 75–78 for $\text{M}=\text{C}$, regardless of the nature of R. For the case of $\text{R}_1\text{R}_2\text{CH}$ bonded to $(\text{CH}_3)_3\text{M}$ we observe 60 $\text{kcal}\cdot\text{mole}^{-1}$ for $\text{M}=\text{Sn}$ and 72–73 $\text{kcal}\cdot\text{mole}^{-1}$ for $\text{M}=\text{C}$, again independent of the nature of R_1 and R_2 . Finally, another decrease in the dissociation energy is observed when $\text{R}_1\text{R}_2\text{R}_3\text{C}$ is bonded to both Sn and C. CH_3 is a unique case and is the strongest bond to M in both Sn and C compounds.

It is also to be noted that the average thermochemical bond energies are a very poor approximation to the actual bond dissociation energies, having values 17 $\text{kcal}\cdot\text{mole}^{-1}$ smaller than the actual dissociation energies. From the measured energies of dissociation of the first bond, *viz.*:



and the total thermochemical bond energy of the molecule we find the average C-Sn bond energy in the $(\text{CH}_3)_3\text{Sn}$ radical to be only 44 $\text{kcal}\cdot\text{mole}^{-1}$. Thus in thermal decompositions of trimethylalkylstannanes the tin atoms should have a tendency to lose all their alkyl groups.

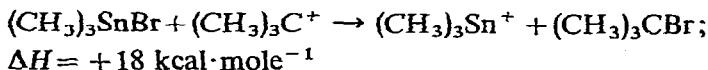
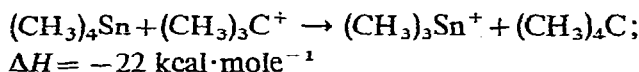
Ionization potential of (CH₃)₃Sn

An indirect evaluation of the ionization potential of the (CH₃)₃Sn radical may be obtained as the difference between the heats of formation of (CH₃)₃Sn⁺ and (CH₃)₃Sn. The value we find is $I_2[(\text{CH}_3)_3\text{Sn}] = 158 \pm 7 \text{ kcal} \cdot \text{mole}^{-1}$ or $I_2[(\text{CH}_3)_3\text{Sn}] = 6.8 \pm 0.3 \text{ eV}$. Recently, using a double-pulsed mass spectrometric method in which radicals were formed by the impact of one electron beam on (CH₃)₃Sn-Sn(CH₃)₃ and ionized by a second electron beam, Lampe and Niehaus⁴¹ have carried out a direct measurement of the vertical ionization potential of (CH₃)₃Sn and have reported a value of $I_2[(\text{CH}_3)_3\text{Sn}] = 7.10 \pm 0.05 \text{ eV}$ to be compared with our indirect value of $6.8 \pm 0.3 \text{ eV}$. In the work of Lampe and Niehaus⁴¹ no attempt was made to use a monoenergetic electron beam and it has recently been shown⁴²⁻⁴⁵ that radical ionization potentials determined with electron beams of large energy spread are probably high by 0.2-0.5 eV. We therefore view our indirectly measured value of $6.8 \pm 0.3 \text{ eV}$ as being in excellent agreement with the directly measured value. This agreement lends a considerable degree of confidence to our measured heat of formation of the (CH₃)₃Sn radical and thus to the bond dissociation energies.

HEATS OF FORMATION OF IONS

As mentioned already, the heat of formation of the (CH₃)₃Sn⁺ ion is 190 kcal·mole⁻¹. The molecular ionization potentials in Table 2 are easily convertible to heats of formation of the (CH₃)₃SnX⁺ ions, since with the assumption of no excess energy in the ionization process, the ionization potential is simply the difference between the heats of formation of (CH₃)₃SnX⁺ and (CH₃)₃SnX. As discussed in the experimental section, there is an ambiguity in the identity of the ions labelled (CH₃)₂-SnX⁺ since a CH₃ may be lost from the alkyl groups instead of from the Sn. Only in the case of (CH₃)₃Sn-C₂H₃ and (CH₃)₃Sn-CH₂(CH₃)₂⁺ can we be reasonably sure of the identity of the (CH₃)₂SnX⁺ ion. For this reason we have not thought it worthwhile to convert the appearance potentials in the last column of Table 2 to heats of formation.

One method of assessment of the relative stabilities of stannyl cations to the corresponding carbon cations is to compare the enthalpy changes for chemical reactions involving analogous carbon and stannyl compounds. As an example we have the two typical reactions for (CH₃)₃M⁺ ions:



The conclusion from this is that in equilibria (at least in the gas phase) between analogous trimethylstannyl and tert-butyl cations and their molecular precursors, the trimethylstannyl ions are energetically favored, except when unusually strong bonds to the Sn (such as to highly electronegative groups) must be broken. In this latter case the carbonium ion is energetically favored.

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