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STUDIES ON THE UNIMOLECULAR DECOMPOSITION PROCESSES OF ORGANOMETALLIC IONS

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Summary

The ionic decomposition processes of dimethyl derivatives of the Main Group IV elements (Me_2SiH_2, Me_2GeH_2 and Me_2SnH_2) were studied by means of mass spectrometry and He(I) photoelectron spectroscopy. The second derivatives of the total ion currents obtained by numerical differentiation were compared to the He(I) photoelectron spectra in the region of low energy excitation. QET calculations of 70 eV mass spectra were also performed. The results obtained do not show inconsistencies with the statistical theory.

I. Introduction

The unimolecular dissociation processes taking place in the ion source of a mass spectrometer can be interpreted on the basis of the statistical theory often referred to as RRKM or QET * [1,2]. This theory has been successfully applied in the evaluation of ionic dissociation rate constants, breakdown diagrams and 70 eV mass spectra [4–6]. Because of this success, it has been possible to use the theory to determine whether electronic as well as vibrational energy is randomized. In certain cases (e.g. hydrocarbons investigated so far) the statistical behaviour seems to be supported by experimental tests. On the other hand, non-statistical fragmentations have also been reported in the literature [7–9].

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* RRKM = Riece–Ramsperger–Kassel–Marcus theory.
QET = quasi equilibrium theory.

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Organometallic compounds appear to be an interesting class of molecules for the investigation of unimolecular decay processes. Photoelectron spectroscopic studies show [10,11] that removing electrons from the metal atoms or the metal–carbon bonds results in well-separated electronic states. The distinct difference between electronic states associated with the metal and the hydrocarbon groups will probably result in very little coupling, or interaction, between them. Large differences in bond energies and vibrational frequencies between metal–carbon and carbon–carbon bonds are also expected to inhibit the free flow of vibrational energies.

Given these circumstances, it seems to be reasonable to study the ionic unimolecular decompositions of organometallic compounds in detail. The model compounds chosen here are analogous to propane, which was thoroughly studied in earlier QET calculations [12].

In this paper we report studies on the ionic decomposition processes of dimethyl derivatives of the Main Group IV elements (Me_2SiH_2, Me_2GeH_2, Me_2SnH_2). These studies are based on electron-impact mass spectroscopic and UV photoelectron spectroscopic experiments.

Experimental

Materials

Dimethylsilane (I), dimethylgermane (II) and dimethyltin (III) were prepared by reduction of their corresponding halogen derivatives with $LiAlH_4$ in ether [13,14]. The purity was checked by GLC, and trap-to-trap distillation was made where necessary.

Instrumentation

The mass spectrometric measurements were performed with an Atlas CH4 instrument. The samples were introduced via a gas inlet system. At the normal operating temperature of the ion source (~ 150 °C), there was no indication of thermal decomposition of the compounds. Ionization energies were determined by the methods of Honig [15] and Lossing et al. [16] and the appearance energies by the Warren method [17]. Xenon was introduced with the sample to calibrate the electron energy.

The photoelectron spectra were recorded on a Perkin–Elmer PS18 spectrometer and calibrated against Ar and Xe lines. The estimated error in the IE values is between ± 0.05 and ± 0.1 eV.

Calculations

The QET calculations were performed on a CDC-3300 computer by using a program written in Fortran language. The relative intensities of secondary ions were also calculated by this program. The values of $k_i(E)$ were calculated at values of E from 0 to 8.0 eV at intervals of 0.2 eV. This energy range matches well with the accessible ionic states represented by the PE spectrum.

The second derivatives of the ionization efficiency (SDIE) curves were obtained by numerical differentiation of the respective experimental data. Being aware of the well-known theoretical and practical difficulties related with numerical differentiation, we checked several algorithms of different types. The following one proved to be numerically stable when tested on artificial data simulating simple analytical functions. In order to improve the noise/signal ratio and numerical stability, data were smoothed and interpolated resulting in equidistant separation (of 0.05 eV).

For interpolation, the standard Lagrange method was used, accompanied with a smoothing with a parabolic spline function over 5 data points. After this preparation the data base was repeatedly smoothed 2–4 times using a parabolic spline over 5–7 data points. Numerical differentiation was carried out by Savitzky's method [18] using quadratic polynomials fitted to 7 data points.

Results and discussion

Photoelectron spectra

The photoelectron spectra of I (Me_2SiH_2), II (Me_2GeH_2) and III (Me_2SnH_2) are presented in Fig. 1 and the ionization energies related to the first band are summarized in Table 1.

The main feature of the spectra is that they show two well-separated bands. The

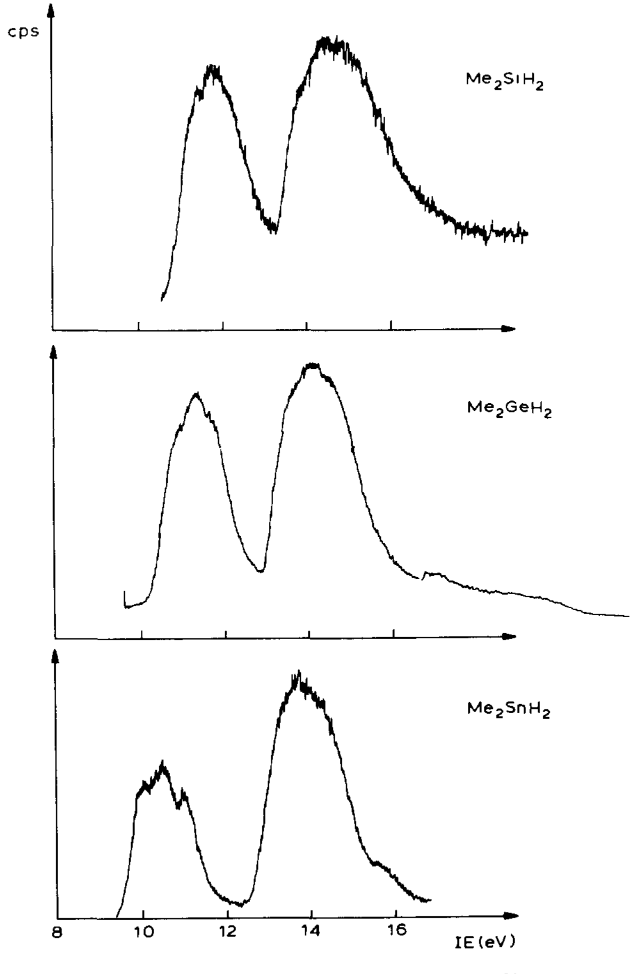

Fig. 1. Photoelectron He(I) spectra of Me_2XH_2 (X = Si, Ge and Sn).

TABLE 1

THE FIRST THREE IONIZATION ENERGIES (eV) FOR THE DIMETHYL DERIVATIVES OF THE GROUP IV ELEMENTS FROM THEIR PE SPECTRA

Compound	IE_1	IE_2	IE_3	Ref.
Me_2SiH_2	11.2	11.5	11.8	[10]
Me_2GeH_2	10.8	11.2	11.6	This work
	10.7	11.0	11.5	[18]
Me_2SnH_2	10.0	10.5	11.0	This work

first band, composed by three overlapped peaks, can be assigned to the metal–carbon and metal–hydrogen bonds while the second one can be connected with the ionization of the C–H bonds.

The assignment of the Me_2SiH_2 orbitals has previously been reported [10]; the three local maxima of the first PE band were assigned to the $4b_1$, $6a_1$ and $2b_2$ orbitals. Drake et al. [19] studied the He(I) and He(II) PE spectra of the Me_2GeX_2 (X = H, F, Cl) series. Their assignment supported by CNDO/2 calculations showed that in the case of Me_2GeH_2 the uppermost molecular orbitals are those of germanium–carbon and germanium–hydrogen ($3b_1 > 4a_1 > 3b_2$). This orbital sequence is in agreement with that of Me_2SiH_2. The same order of orbitals can be suggested for Me_2SnH_2 and is supported by the regular decrease in ionization energies (see Table 1).

In contrast, the PE spectrum of propane shows overlapped bands which are not separated by large energy gaps [20].

So one can conclude that replacement of the central carbon atom in propane by a metal atom results in ionic states of low energy. Obviously this is reflected by the electron-impact mass spectra.

Mass spectra

The 70 eV, monoisotopic mass spectra of I–III as well as that of propane are shown in Fig 2. The mass spectra of I–III differ in several respects from that of propane [12]:

(i) The intensity of the parent ion is very weak.

(ii) The fragment ions $P^+ - 1$ and $P^+ - 2$ are formed in competitive reactions by the breakage of metal–hydrogen bond(s). This is clearly shown by the mass spectrum of Me_2SnD_2 and those of R_3SiH-type compounds where no fragments are formed by the loss of 2 a.m.u. [21]. In the case of propane, there is no preferential hydrogen loss from the central carbon atom.

(iii) The mass spectra of compounds analogous to propane show intensive X^+ (Si^+, Ge^+ and Sn^+) ions, so that fragmentation occurs via consecutive and competitive X^+–H and X^+–C bond fissions. All of these characteristics could be ascribed to a preferential charge localization on the metal atom.

Ionization efficiency (IE) curves

The *IE* curves for the fragments of I, II and III are shown in Figs. 3–5; the ionization (*IE*) and appearance energies (*AE*) are summarized in Table 2. The *AE* values for Me_2GeH_2 were not reproducible so they are excluded from Table 2.

The parent ion of $Me_2SnH_2{}^+$ is of very low intensity which is why we could not determine its electron-impact ionization energy. This value was estimated with the

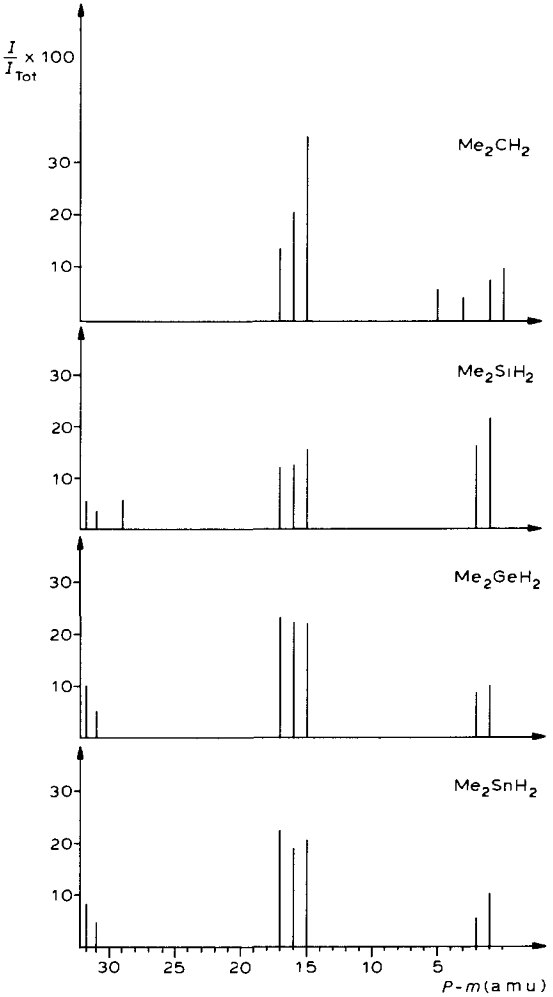

Fig. 2. 70 eV mass spectra of Me_2XH_2 (X = C, Si, Ge and Sn). Me_2CH_2 taken from ref. 12.

TABLE 2

ELECTRON-IMPACT IONIZATION (*IE*) AND APPEARANCE ENERGIES (*AE*) IN eV FOR Me_2SiH_2 AND Me_2SnH_2

Ions	*IE* or *AE* (eV)	
	X = Si	X = Sn
$Me_2XH_2^+$	10.7	8.9[a]
Me_2XH^+	11.1	10.4
Me_2X^+	10.9	9.9
$MeXH_2^+$	11.5	10.6
$MeXH^+$	11.0	9.8
MeX^+	14.0	10.9
X^+	14.5	10.4

[a] Estimated by linear extrapolation (see text).

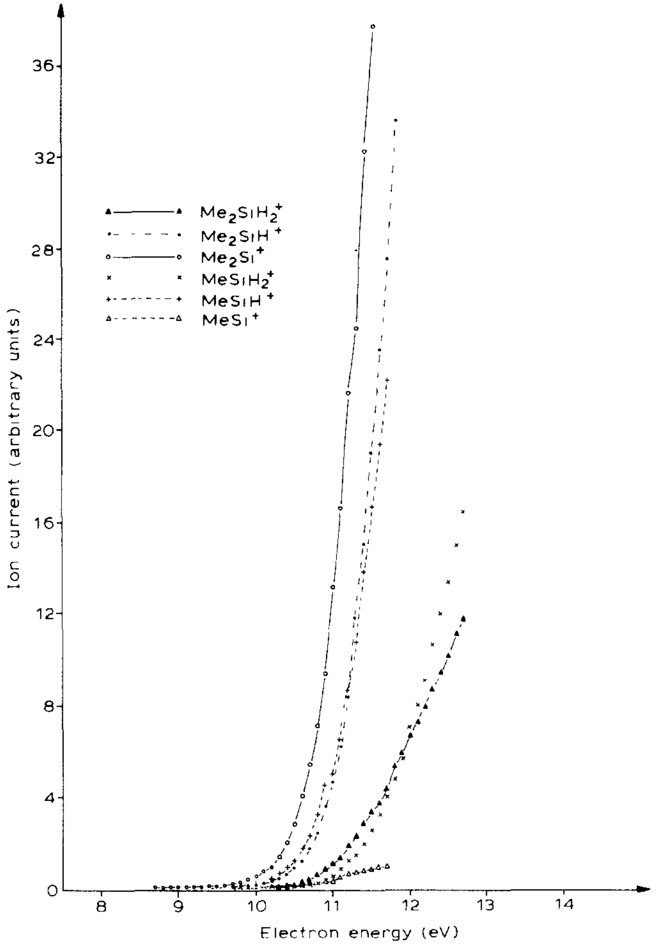

Fig. 3. Ionization efficiency curves for ions formed from $Me_2SiH_2^+$.

help of its photoelectron spectrum. For this reason we determined the correlation between electron-impact *IE*'s and the first ionization energies obtained from the PE spectra. In the case of XH_4 (X = C, Si, Ge, Sn) [22–24] and XMe_4 (X = Si, Ge, Sn) [25,26], we found a good linear correlation (correlation coefficients are 0.988 and 0.982, respectively) between the electron-impact and photon-impact first ionization energies determined from the PE spectrum. By suggesting the same linear correlation for the dimethyl derivatives, we constructed the *IE* (photon impact) vs. *IE* (electron impact) curve using the corresponding values for Me_2CH_2 and Me_2SiH_2. The electron-impact *IE* of Me_2SnH_2 was then determined by linear extrapolation. Its value was found to be 8.9 ±0.1 eV.

Second derivatives of the total ion current

The statistical theory of mass spectra assumes that molecular ions are formed in different energy states upon ionization so that excitation energies in excess of the

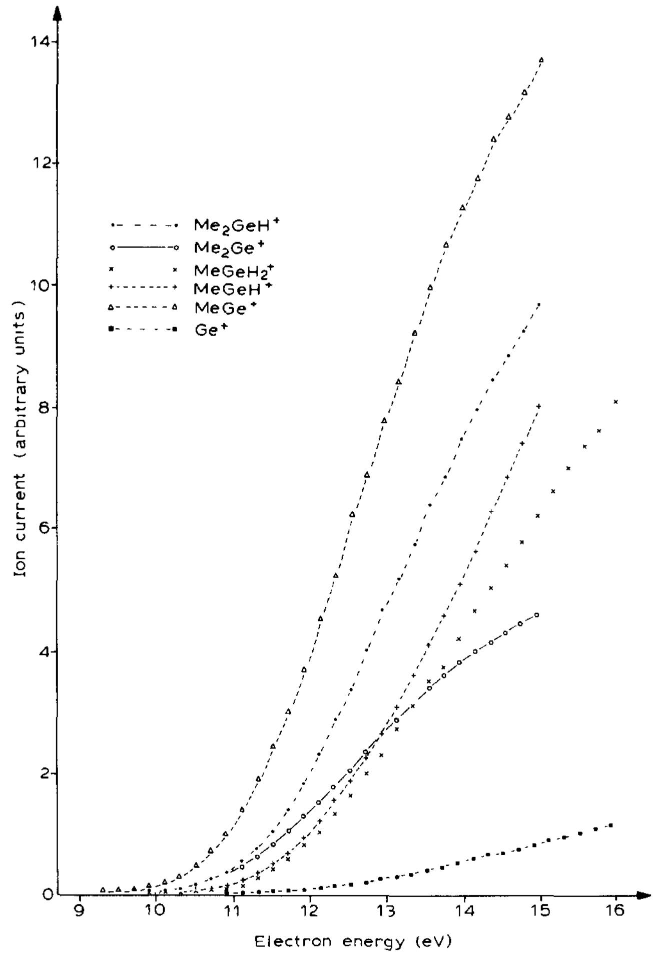

Fig. 4. Ionization efficiency curves for ions formed from $Me_2GeH_2^+$.

adiabatic ionization energy show a distribution. This distribution function is the energy deposition function, *P*(ED).

The internal energy distribution, *P*(E), of the ion is given by the convolution integral of *P*(ED) and the Boltzman thermal energy distribution. An experimental approach to the determination of *P*(E) is the measurement of the energy deposition function, *P*(ED) [27]. A reasonable estimate of *P*(ED) can be obtained from the second derivative of the electron-impact total ionization efficiency curve [28–31]. This function can be used in calculating the 70 eV mass spectra. Furthermore, its general structure may be considered evidence for energy randomization (internal conversion to the electronic ground state) [32].

Unfortunately, the scatter of the second derivative becomes quite large about 3–5 eV above the threshold, as shown by Chupka and co-workers [33,34] which makes the excitation of higher states indicated by the photoelectron spectra difficult to study. Figure 6 shows the second derivative of the total ion current for I–III together with the appropriate part of the photoelectron spectrum. In Fig. 7 the *IE* curve of

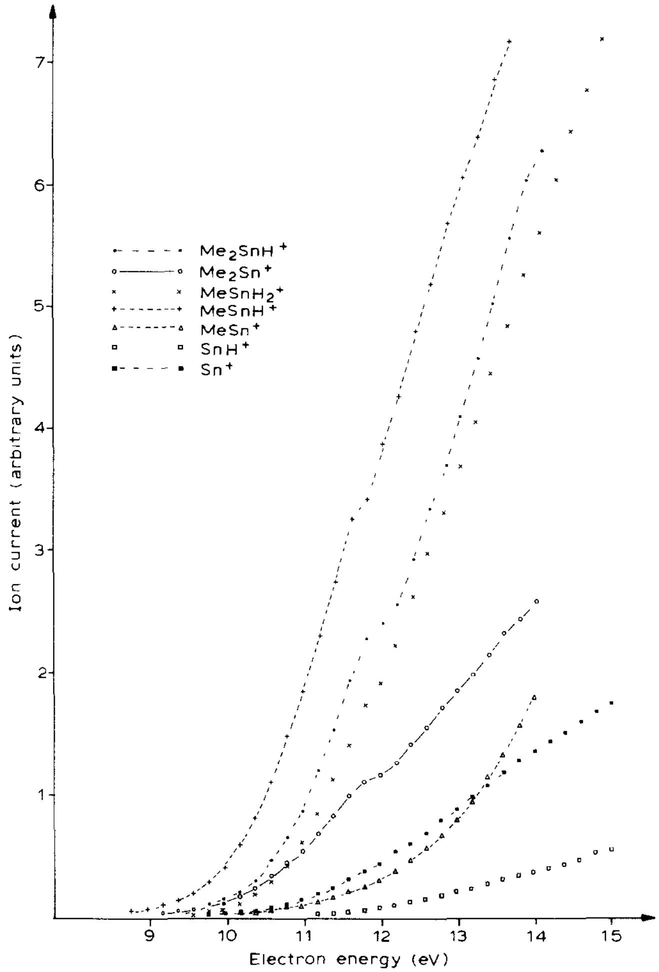

Fig. 5. Ionization efficiency curves for ions formed from $Me_2SnH_2{}^+$.

Xe^+ (used as internal standard) and its second derivative can be seen. The second derivative of the total ion current of *I* is not complete and does not exceed 1.5 eV above the threshold. The reason for this is that the corresponding *IE* curves were run in order to determine the fragment appearance energies. These curves become linear in a relatively short energy range which is sufficient for the evaluation of the required data. Comparing the derivative of the total ionization efficiency (SDIE) with the corresponding part of the PE spectrum, it is remarkable that the SDIE shows a well-defined positive value below the photon-impact IE_{ad}. This experimental finding is also characteristic for the other two compounds and can be ascribed to the effect of the electron energy distribution and the internal thermal energy of the parent ion.

The SDIE for II and III shows a number of distinct maxima. It is difficult to determine whether these maxima can be related to ionic states or to a fictitious structure resulting from numerical treatment of the experimental data. The former

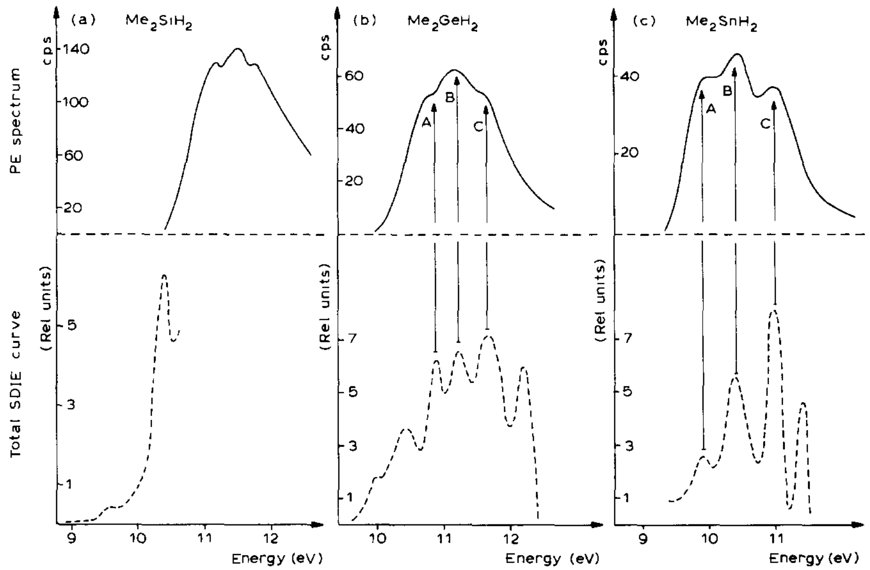

Fig. 6. The first band of the He(I) photoelectron spectra and plots of d^2I_{tot}/dE^2 vs. electron energy for Me_2XH_2 (X = Si, Ge and Sn).

suggestion is supported by the close correspondence with certain peaks in the PE spectrum (A,B,C in Figs. 6b and 6c) and by the regular shape of the SDIE for Xe^+ (Fig. 7).

On the other hand, the serious fluctuation of the second derivatives of the total ion current and that of the fragments (not shown here) at ca. 5–6 eV above the ionization threshold cast doubt on the reliability of this structure.

QET calculation

The assumption concerning the statistical behaviour of the compounds studied can be checked by calculating the 70 eV mass spectra, although agreement between predicted and experimental mass spectra is a necessary though not a sufficient criterion for its validity. Since this work may regarded as a qualitative attempt, the classical harmonic oscillator model [3] seemed to be sufficient for calculating the 70 eV mass spectra. The calculations were performed for the case of I and III; as mentioned previously, the appearance energies for Me_2GeH_2 were not available because of experimental difficulties. The fragmentation scheme of dimethylsilane and dimethyltin is rather simple; the primary processes can be summarized in the following scheme:

$$(CH_3)_2XH_2^{\cdot +}\ (X=Si, Sn)\ \xrightarrow{(1)} (CH_3)_2XH^+ + H^\cdot$$

$$\xrightarrow{(2)} (CH_3)_2X^{\cdot +} + H_2$$

$$\xrightarrow{(3)} CH_3XH_2^+ + CH_3^\cdot$$

$$\xrightarrow{(4)} CH_3XH^{\cdot +} + CH_4$$

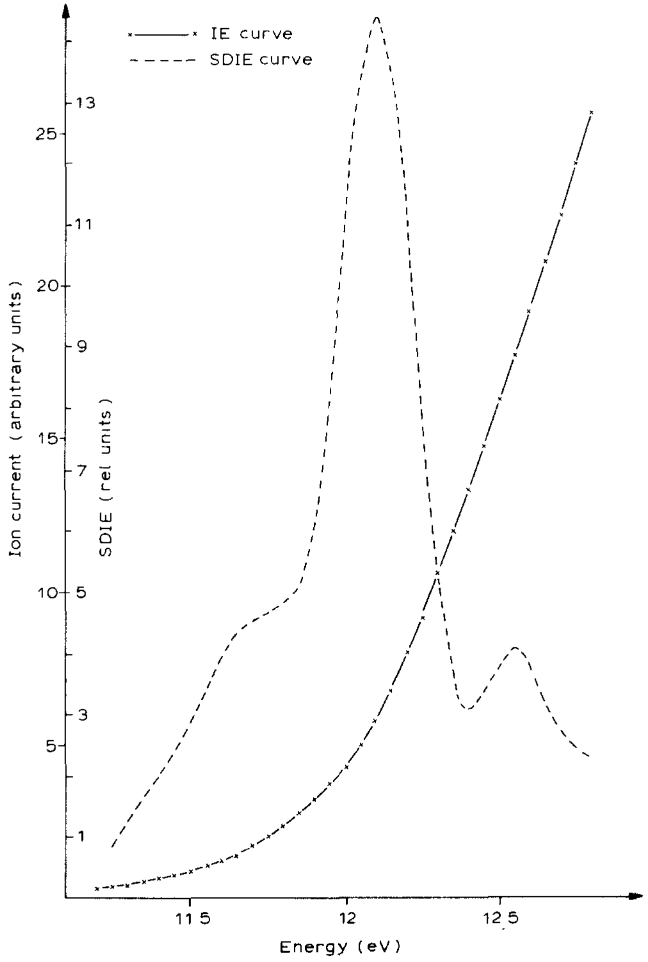

Fig. 7. Ionization efficiency and SDIE curves for Xe^+.

The assumption that H_2 and CH_4 are formed in reactions 2 and 4 respectively is substantiated by the *AE* data.

The input parameters of calculations giving the best agreement with the experimental mass spectra are summarized in Table 3, in which the number of internal degrees of freedom is not included. This parameter was taken equal to 9 by considering the methyl groups as single mass points.

The critical energy for primary product ions, E_b, necessary to undergo secondary decomposition with $k = 10^6\ s^{-1}$ was calculated by the known equation [35]:

$$E_b = (n_b/n_a)(E_a - \epsilon_p + \Delta H_r)$$

where n_a is the number of internal degrees of freedom in the reactant molecular ion of the primary reaction, n_b is the number of internal degrees of freedom in the ionic product of the primary reaction, ϵ_p is the activation energy of the primary reaction in the forward direction, $\Delta\ H_r$ is the activation energy for the reverse process, and E_a is the internal energy of the parent ion.

TABLE 3

INPUT PARAMETERS USED IN THE QET CALCULATIONS FOR THE DECOMPOSITION OF DIMETHYLSILANE AND DIMETHYLTIN

Compound	Reaction No.	Reaction coordinate	Frequencies changed in the activated complex (cm^{-1})	Reaction degeneracy	Activation energy (eV)
Me_2SiH_2	1	ν_3/q(Si-H)	ν_9^*/γ(C–Si–C) 70	2	0.4
	2	ν_3/q(Si-H)	–	1	0.2
	3	ν_{21}/q(Si-C)	ν_{26}^*/β(H–Si–C) 100 ν_9^*/γ(C–Si–C) 70	2	0.8
	4	ν_{21}/q(Si-C)	–	2	0.3
Me_2SnH_2	1	ν_3/q(Sn-H)	ν_9^*/γ(C–Sn–C) 50	2	1.5
	2	ν_3/q(Sn-H)	–	1	1.0
	3	ν_{21}/q(Sn-C)	ν_{13}^*/β(H–Sn–C) 100 ν_9^*/γ(C–Sn–C) 50	2	1.7
	4	ν_{21}/q(Sn-C)	–	2	0.9

TABLE 4

OBSERVED AND CALCULATED 70 eV MASS SPECTRAL DATA OF DIMETHYLSILANE AND DIMETHYLTIN (FRACTIONAL ABUNDANCE)

Me_2SiH_2 Ion	I_{obs}	I_{calcd}	Me_2SnH_2 Ion	I_{obs}	I_{calcd}
Me_2SiH^+ SiH_3^+	30.5	43.9	Me_2SnH^+	18.2	10.2
			Me_2Sn^+	6.0	10.3
Me_2Si^+	18.7	24.8	$MeSnH_2^+$	18.1	21.8
$MeSiH_2^+$	17.2	10.8	$MeSnH^+$	13.3	19.5
$MeSiH^+$ Si^+	20.1	8.7	$MeSn^+$	28.9	27.8
			Sn^+	15.5	10.4
$MeSi^+$	13.5	11.8			

As far as the relative intensity of secondary ions is concerned, the best agreement with experiments was found when all internal degrees of freedom were taken to be active in the term n_b/n_a.

The final step in the calculation of the 70 eV mass spectrum is weighting the relative ion abundances according to the internal energy distribution function which was approximated by the He(I) photoelectron spectrum. The results are shown in Table 4.

Conclusions

The main aim of this study was to investigate the applicability of the statistical theory to the ionic unimolecular decomposition of organometallic compounds analogous to propane. The analysis of the second derivative of the total ion current shows that qualitative agreement exists between ionic states corresponding to the first PE band and those formed by electron impact in the same energy region. Unfortunately, the higher energy part of the SDIE curve cannot be evaluated as a consequence of its scatter.

The question as to whether the energy of higher states, formed by ionization of C–H bonds composing the second PE band and separated by ca. 1 eV from the first band, is converted to the vibrational energy of the ground state is far from answered. However, in the calculations the whole PE spectrum has been used so that it is assumed that the energy of the electronic states formed by the ionization of the C–H orbitals is available for fragmentation. This is some indication of an energy randomization through all the accessible states. The results of QET calculations performed by using the classical harmonic oscillator model show semiquantitative agreement with the experiments.

Although there is no doubt concerning the approximate feature of this type of calculation [36], some importance can be attributed to the fact that the same principles were used in all of the calculations.

The estimation of the transition state configuration, the reduction in the effective number of oscillators, and the approximation of $P(E)$ by the He(I) PE spectrum were performed in the same manner in both calculations. We tried to apply several variations of the activated complex configuration. The frequencies shown in Table 3 correctly reflect those characteristics (loose and tight activated complex) which can be associated with reactions occurring via single bond breakage or rearrangement. Summarizing our results, we can conclude that our qualitative data do not show inconsistencies with the statistical theory.

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