

On the structure of some electron impact induced fragmentation products of $\text{Si}(\text{C}_6\text{H}_5)_4$, $\text{Ge}(\text{C}_6\text{H}_5)_4$ and $\text{Sn}(\text{C}_6\text{H}_5)_4$ *

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Abstract

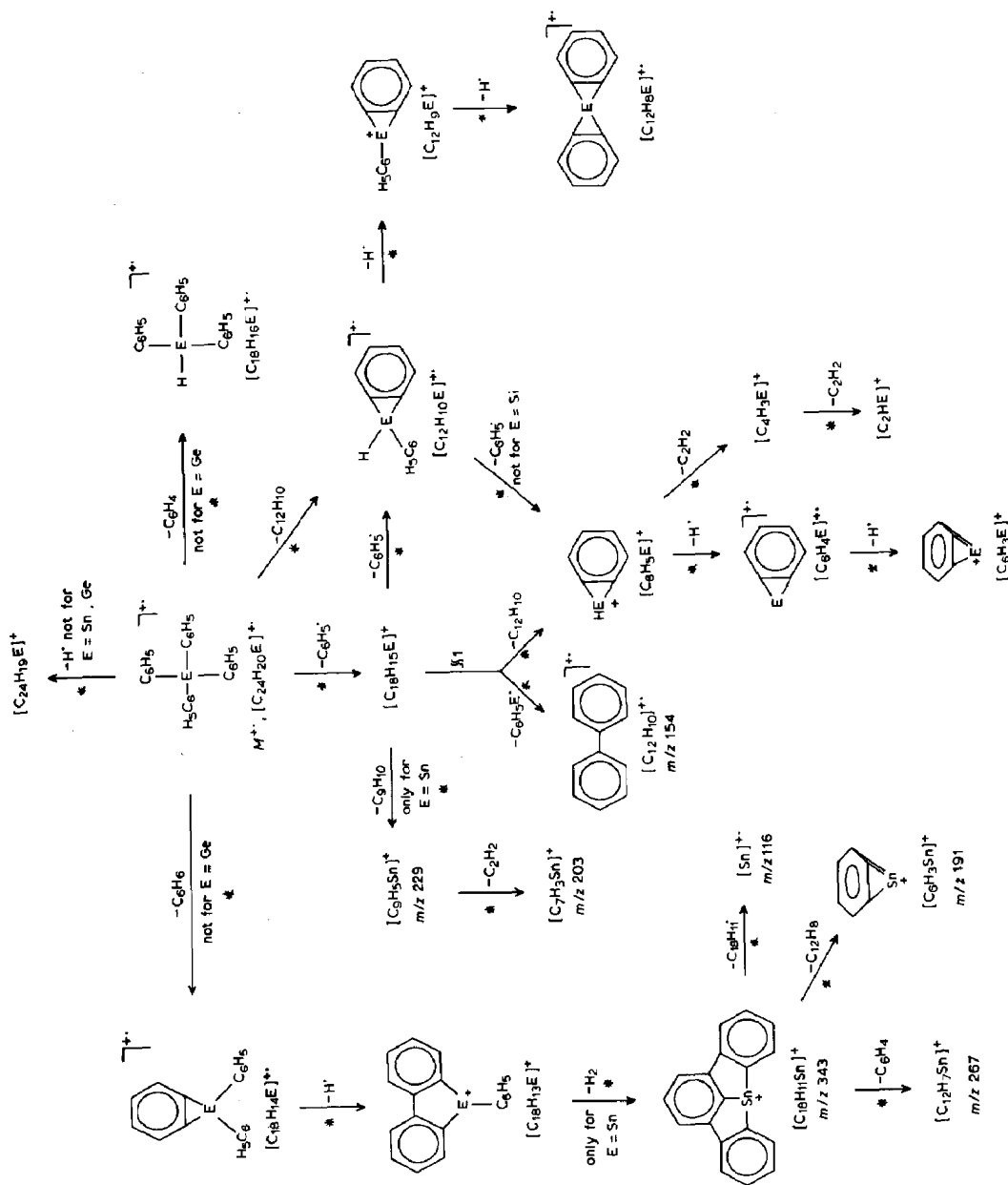
The electron impact mass spectrometric behaviour of tetraphenyl derivatives of Si, Ge and Sn is discussed on the basis of results of exact mass measurements, linked scans, mass analysed ion kinetic energy spectrometry, and collisional experiments. The possible structures of fragment ions are discussed, and the relevance of the findings to solution chemistry is considered.

Introduction

By far the largest scale manufacture of organometallic compounds involves group 4 compounds which have a wide range of technical applications [1]. The tetraorgano derivatives of the group 4 elements have no significant direct application, but they are important as intermediates in the manufacture of the species $\text{R}_n\text{EX}_{4-n}$ (E = Si, Ge, Sn) and the variations in reactivity and relationships between chemical and spectroscopic properties of the tetraalkyl and tetraaryl derivatives of the group have been extensively investigated [2].

In particular, mass spectrometry has proved to be a useful tool for elucidating the structure or reactivity of these gaseous organometallic compounds. It has been emphasized that under electron impact (EI) conditions, the tetraalkyl and tetraaryl derivatives give molecular ions in only low abundance and loss of alkyl or aryl radicals represent the most favoured decomposition pathway [3-5]. Furthermore the

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Scheme 1

Table 1

m/z values and relative abundances of the predominant ionic species arising for EI of 1-3; kinetic energy $T_{1/2}$ (meV) related to the discussed fragmentation pathways. (The m/z values refer to ^{28}Si , ^{70}Ge and ^{116}Sn ; the ^{70}Ge and ^{116}Sn isotopes were chosen to avoid overlap of the various ionic species).

Ionic species	1 (Si)			2 (Ge)			3 (Sn)		
	Elemental composition	m/z (rel.ab)	$T_{1/2}$	m/z (rel.ab)	$T_{1/2}$	m/z (rel.ab)	$T_{1/2}$		
$[M]^{++}$	$[\text{C}_{24}\text{H}_{20}\text{E}]^{++}$	336(32)	-	378(3)	-	424(0.5)	-		
$[M-H]^+$	$[\text{C}_{24}\text{H}_{19}\text{E}]^+$	335(1)	-	-	-	-	-		
$[M-C_6H_4]^{++}$	$[\text{C}_{18}\text{H}_{16}\text{E}]^{++}$	260(100)	-	-	-	348(73)	-		
$[M-C_6H_3]^+$	$[\text{C}_{18}\text{H}_{15}\text{E}]^+$	259(15)	26 meV	301(28)	235 meV	347(100)	194 meV		
$[M-C_6H_6]^{++}$	$[\text{C}_{18}\text{H}_{12}\text{E}]^{++}$	258(12)	-	-	-	346(4)	-		
$[M-C_{12}H_{10}]^{++}$	$[\text{C}_{12}\text{H}_{10}\text{E}]^{++}$	182(62)	113 meV	224(14)	50 meV	270(30)	182 meV		
$[(M-C_6H_5)-C_6H_5]^{++}$	$[\text{C}_{12}\text{H}_{10}\text{E}]^{++}$	182(62)	312 meV	224(14)	230 meV	270(30)	102 meV		
$[(M-C_6H_5)-C_{12}H_{10}]^{++}$	$[\text{C}_6\text{H}_5\text{E}]^{++}$	105(18)	451 meV	147(14)	407 meV	193(50)	220 meV		
$[(M-C_6H_5)-C_6H_5\text{Me}]^{++}$	$[\text{C}_{12}\text{H}_{10}]^{++}$	154(4)	-	154(100)	-	154(45)	-		
$[(M-C_6H_5)-C_9H_{10}]^+$	$[\text{C}_9\text{H}_5\text{E}]^+$	-	-	-	-	229(4)	687 meV		
$[(M-C_6H_5)-C_9H_{10}]-C_2H_2]^+$	$[\text{C}_7\text{H}_3\text{E}]^+$	-	-	-	-	203(1.5)	-		
$[(M-C_{12}H_{10})-H]^+$	$[\text{C}_{12}\text{H}_9\text{E}]^+$	181(25)	-	223(6)	-	269(5)	-		
$[(M-C_{12}H_{10}-H)-H]^+$	$[\text{C}_{12}\text{H}_8\text{E}]^{++}$	180(10)	-	222(2)	-	268(2.5)	-		
$[(M-C_6H_5)-C_{12}H_{10}]-H]^+$	$[\text{C}_6\text{H}_4\text{E}]^{++}$	104(1)	-	146(2)	-	192(2.5)	-		
$[(M-C_6H_5)-C_{12}H_{10}-H]-H]^+$	$[\text{C}_6\text{H}_3\text{E}]^+$	103(3)	-	145(1)	-	191(2.5)	-		
$[(M-C_6H_5)-C_{12}H_{10}]-C_2H_2]^+$	$[\text{C}_4\text{H}_3\text{E}]^+$	79(4)	-	121(2)	-	167(2.5)	-		
$[(M-C_6H_5)-C_{12}H_{10}-C_2H_2]-C_2H_2]^+$	$[\text{C}_2\text{HE}]^+$	53(8)	-	95(6)	-	141(4)	-		
$[(M-C_6H_6)-H]^+$	$[\text{C}_{18}\text{H}_{13}\text{E}]^+$	257(7)	-	-	-	345(5)	-		
$[(M-C_6H_6-H)-H_2]^+$	$[\text{C}_{18}\text{H}_{11}\text{E}]^+$	-	-	-	-	343(7.5)	-		
$[(M-C_6H_6-H-H_2)-C_6H_4]^+$	$[\text{C}_{12}\text{H}_7\text{E}]^+$	-	-	-	-	267(1.5)	233 meV		
$[(M-C_6H_6-H-H_2)-C_{12}H_8]^+$	$[\text{C}_6\text{H}_3\text{E}]^+$	-	-	-	-	191(2.5)	1067 meV		
$[(M-C_6H_6-H-H_2)-C_{18}H_{11}]^{++}$	$[\text{E}]^{++}$	-	-	-	-	116(57)	2699 meV		

dissociation energies for E–C bonds have been evaluated by means of appearance energy (AE) measurements [5], but neither the structures of the ions nor the relationships to the condensed phase chemistry of these compounds were considered. In this paper we describe the EI behaviour of $E(C_6H_5)_4$ ($E = Si, Ge, Sn$, compounds 1, 2 and 3, respectively), as studied by means of metastable ion studies [6,7] and collisional spectroscopy [8], with emphasis on the structures of the ions and the possible relevance to solution chemistry.

Experimental

All mass spectrometric measurements were performed on a VG ZAB2F instrument operating under electron impact (EI) conditions. Metastable transitions were detected by B/E linked scans [6] and mass analyzed ion kinetic energy (MIKE) spectrometry [7]. Collisional experiments [8] were obtained by 8 keV ions colliding with air in the second field-free region.

The pressure in the collision cell was such as to reduce the main beam intensity to 60% of its usual value. The kinetic energy releases were calculated by use of the usual formulae [7]. Exact mass measurements were performed by the peak matching technique at 10000 resolution (10% valley definition). Compounds 1–3 were analytically pure samples purchased from Alfa Ventron (Karlsruhe).

Results and discussion

The common fragmentation pattern of compounds 1–3, as obtained from B/E linked scans and exact mass measurements, is shown in Scheme 1, and the relative abundances of the related ions are reported in Table 1.

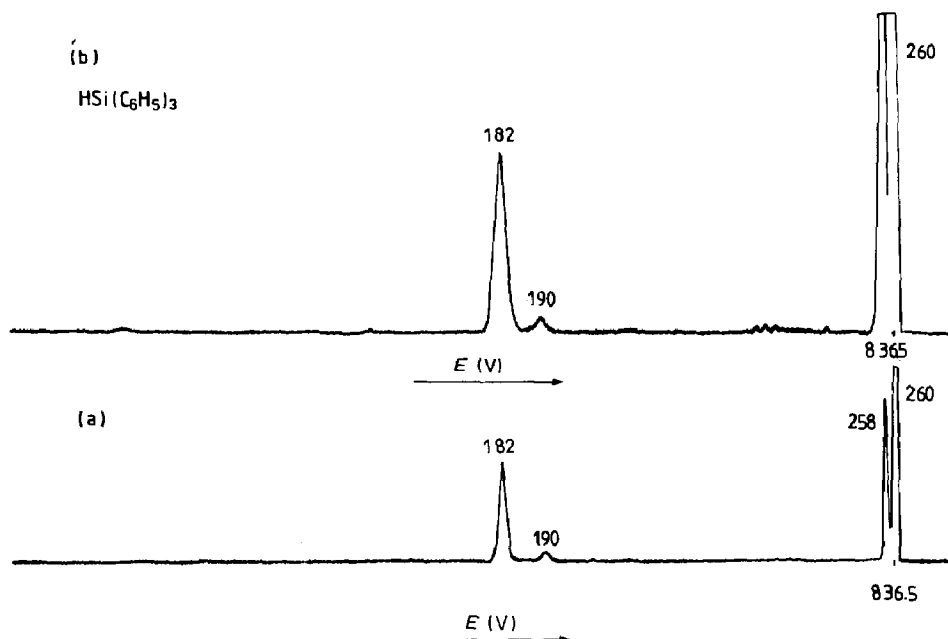


Fig. 1. (a) Collisional spectrum of ionic species at m/z 260 formed by EI on compound 1. (b) Collisional spectrum of M^{++} from Ph_3SiH .

Only compound **1** gives an abundant molecular ion (32%), compounds **2** and **3** giving molecular ions in decreasing abundance (3 and 0.5%, respectively), this behaviour parallels the trend in the mean bond dissociation energies of the E–C bonds of E(CH₃)₄ compounds, which fall on going from Si to Sn [9].

The primary decomposition pathways are due to loss of H (only for E = Si), C₆H₄ (not for E = Ge), C₆H₅, C₆H₆ (not for E = Ge) and C₁₂H₁₀. The H loss, observed for compound **1** only, may reflect a greater stabilization by the (C₆H₅)₃Si group of the resulting [(C₆H₅)₃SiC₆H₄]⁺ ion than is found for the other E(C₆H₅)₃ group (E = Ge, Sn) in the corresponding ions.

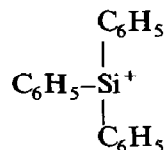
The primary C₆H₄ loss, observed for both compounds **1** and **3**, leads to abundant [C₁₈H₁₆E]⁺⁺ ions, the structure of which was investigated by means of collisional spectroscopy. The collisional spectra of these [M – C₆H₄]⁺⁺ ions are completely superimposable on those of the [M]⁺⁺ ions of the corresponding [EH(C₆H₅)₃]⁺⁺ hydride species used as model compounds (see for example Fig. 1). The abundant loss of H under collision conditions should be noted, since it gives evidence for the hydride structures of the ions under consideration.

The absence of this fragmentation pathway for compound **2** (E = Ge) can be attributed either to a lower proton affinity of Ge than of Si and Sn or to lower stability of the species [GeH(C₆H₅)₃]⁺⁺.

Finally, the particularly high abundance (100%) of this [M – C₆H₄]⁺⁺ ion for compound **1** is significant.

Primary phenyl loss occurs for all the compounds, giving rise to fragment ions of appreciable abundance, and clear differences are present in the kinetic energy releases associated with this decomposition pathway (see Table 1).

While for compound **1** $T_{1/2} = 26$ meV, in agreement with a single bond cleavage and formation of our ionic species with a structure of type a, with the charge



(a)

localized on the silicon atom, for compounds **2** and **3** $T_{1/2}$ goes up to 235 and 194 meV, respectively. This could be due to two effects: either the energy barrier to be

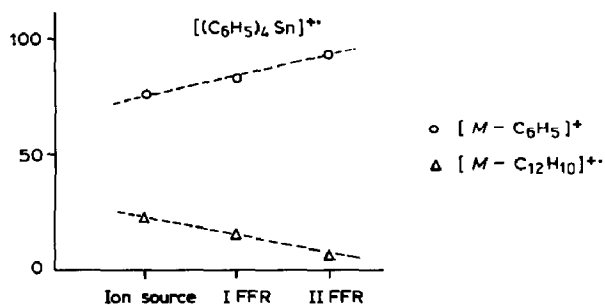


Fig. 2. Absolute abundances of primary [M – C₆H₅]⁺ and [M – C₁₂H₁₀]⁺⁺ fragment ions formed by EI on compound **3**, as observed in the ion source, in the first field-free region (I FFR), and in the second field-free region (II FFR).

overcome forming $[M - C_6H_5]^{++}$ is particularly high, or the product ions are in this case particularly stable thermodynamically. We incline towards the second suggestion, because, even though the E-C bond strength decreases on going from Si to Sn, the formation of highly stable ions with structures different from **a** is clearly confirmed by the further decomposition pathways.

The primary loss of C_6H_6 is observed for compounds **1** and **3** only; this suggests the formation of an *ortho*-metallated moiety such as that shown in Scheme 1.

The last primary decomposition pathway, leading to an abundant fragment ion especially in the case of **1**, is due to $C_{12}H_{10}$ loss. Such fragmentation, well evidenced by metastable ions, indicates either the presence of molecular species with different structures from the neutral molecules, in which the C-C bond is still present, or, alternatively, a concerted loss of two phenyl groups. A comparison of the abundance of fragment ions in the ion source in the first and second field-free regions leads to the estimates of the yields from the decomposition reaction in three different time windows (10^{-7} , 10^{-6} , 5×10^{-6} s, respectively), and hence it can give valuable information about the kinetics of decomposition.

Figure 2 shows the values of the absolute abundances of $[M - Ph]^+$ and $[M - C_{12}H_{10}]^{++}$ ions in the ion source (as obtained from the usual EI spectrum) in the I FFR (as obtained by $B/E = \text{const.}$ linked scans) and in the II FFR (as obtained by MIKE spectrum). These data prove unequivocally that the primary loss of $C_{12}H_{10}$ is a fast process: in fact the abundance of the related fragment is higher for the lower time window. Consequently we conclude that it originates not from a concerted loss of two C_6H_5 moieties (which should be more favoured given longer times), but from molecular species with different structures, such as **b** and **c**.

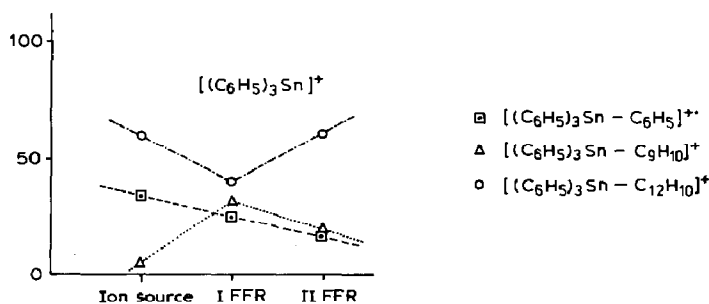
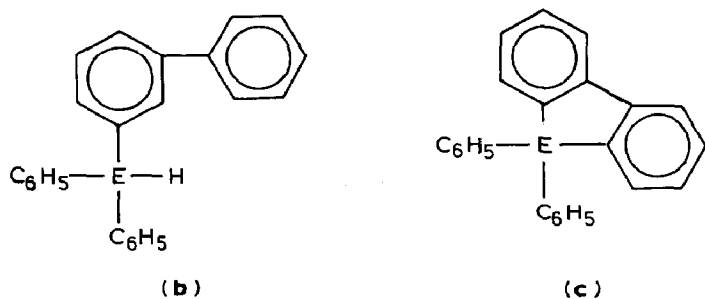


Fig. 3. Absolute abundances of $[(C_6H_5)_3Sn - C_6H_5]^+$, $[(C_6H_5)_3Sn - C_9H_{10}]^+$ and $[(C_6H_5)_3Sn - C_{12}H_{10}]^+$ fragment ions formed by EI on compound **3**, as observed in the ion source, in the first field-free region, (I FFR) and in the second field-free region (II FFR).

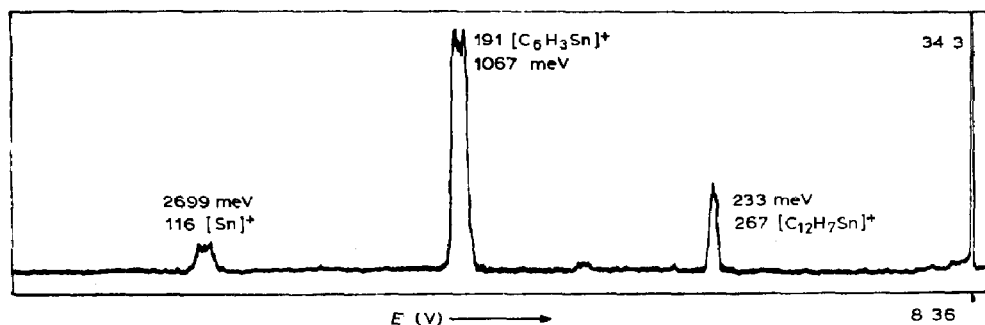


Fig. 4. MIKE spectrum of ionic species at m/z 343 originating from EI of compound 3.

In view of the planarity of the diphenyl moiety, structure **c** must be ruled out, leaving structure **b** as the likely one.

The $[M - C_{12}H_{10}]^{++}$ ions are also generated, as proved by B/E linked scans, through sequential losses of two C_6H_5 . The high kinetic energy values related to the second loss of phenyl (230–312 meV) can be accounted for in terms of the high stability of product ions, for which the benzyne hydride structure shown in Scheme 1 is proposed. The decrease in the $T_{1/2}$ values with the increase in the atomic radius is also relevant in this connection and it must be remembered that analogous derivatives have been synthesized in the condensed phase for $E = Si$.

The $[M - C_6H_5]^+$ ions further decompose through losses of $C_{12}H_{10}$, C_6H_5Me , and C_9H_{10} (the last only for $E = Sn$, compound 3).

The first two losses lead to complementary ionic species, and hence are due to cleavage of the same bond. In this case a structure such as **c** can be proposed, involving a bonded diphenyl moiety. It is interesting to note that the kinetic energy released for the $C_{12}H_{10}$ loss is inversely related to the atomic radius, suggesting that the coordination is more important for smaller atoms than for the larger ones.

An unusual loss of C_9H_{10} is observed for compound 3 only, leading to ionic species at m/z 229. The $T_{1/2}$ value for this fragmentation pathway is 687 meV, indicating the high stability of the product ion.

The $[C_{18}H_{14}E]^{++}$ ions, formed by primary benzene loss, decompose further by H loss to give the fragment ion whose proposed structure is shown in Scheme 1. Only for $E = Sn$ is a further H_2 loss observed, leading to ionic species at m/z 343.

While the C_6H_5 loss is favoured in the ion source (see Fig. 3), losses of C_9H_{10} and $C_{12}H_{10}$ have concurrent kinetics, proving that they originate from cleavages of the same moiety.

The proposed structure is confirmed by the MIKE spectrum (see Fig. 4), which shows losses of C_6H_4 , $C_{12}H_8$ and $C_{18}H_{11}$. The related $T_{1/2}$ values (233, 1067, 2699 meV, respectively) are in agreement with such a structure.

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