

Mass Spectra of Organo-germanes and -stannanes

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MASS SPECTRA of tetraorgano-derivatives of Ge, Sn, and Pb have been little studied,¹ due largely to the polyisotopic nature of the metals which often

results in overlapping patterns making interpretation difficult except under high resolution. We report on the mass spectra of six organostannanes

and a variety of organogermanes at 70eV on an A.E.I. M.S.9 instrument using a resolution better than 1 in 10,000.

In all cases low-intensity molecular ions are observed, for example in the compounds $\text{Ph}_n\text{SnEt}_{4-n}$ ($n = 0-4$) the parent-ion decomposition probability is between 0.9864 and 0.9995.

One generalisation which emerges is that the

hydride ion Et_2MH^+ . Ethyl-Ge and -Sn compounds show intense metastable peaks corresponding to ethylene elimination ($\text{R}_2\text{M}-\text{Et}^+ \rightarrow \text{R}_2\text{MH}^+ + \text{C}_2\text{H}_4$) and this is the major process leading to metal hydride ions in ethylphenyl compounds (Table 2). The tetraphenyls, Ph_4Sn and Ph_4Ge , differ from the tetraethyls in that the R_2M^+ ion is present and for tin it is the fourth most abundant ion.

TABLE 1

Abundance of R_4Sn^+ and R_3Sn^+ ions relative to total tin-containing ions

Compound	% R_4Sn^+	% R_3Sn^+			
		Ph_3Sn^+	Ph_2EtSn^+	PhEt_2Sn^+	Et_3Sn^+
Ph_4Sn	0.12	44.45			
Ph_3SnEt	0.05	62.33	0.47		
Ph_2SnEt_2	1.35		50.8	1.14	
PhSnEt_3	0.26			29.63	0.61
Et_4Sn	0.96				26.19

TABLE 2

Abundance of Sn^+ , SnH^+ , SnH_2^+ , and SnH_3^+ ions relative to total tin-containing ions.

Compound	% Sn^+	% ($\text{SnH}^+ + \text{R}_2\text{SnH}^+$)*	% RSnH_2^+	% SnH^+
SnPh_4	19.17			
SnPh_3Et	13.38	2.02		
SnPh_2Et_2	9.66	16.69	0.88	
SnPhEt_3	9.78	20.19	10.63	
SnEt_4	4.88	36.27	17.27	1.31

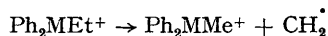
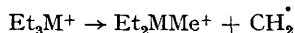
* RSnH^+ and R_3SnH^+ absent.

most abundant species are those in which Sn or Ge is bonded to three or one other groups (alkyl, aryl, or hydrogen). With tin the heaviest fragments, R_3Sn^+ , are also the most abundant, but decrease with increasing ethyl content (Table 1). With organogermanes R_3Ge^+ is generally the most abundant ion but one exception is Et_4Ge where Et_2GeH^+ , formed by the process, $\text{Et}_3\text{Ge}^+ \rightarrow \text{Et}_2\text{GeH}^+ + \text{C}_2\text{H}_4$, is the most abundant ion.

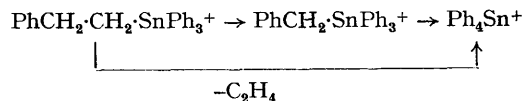
The mixed ethylphenyl-Sn and -Ge compounds produce two R_3M^+ ions, the most abundant being that containing the most phenyl groups. This is expected because ethyl-containing metal ions have a highly favourable mode of decomposition available (ethylene elimination). Moreover it is also observed that the abundance of, for example, Ph_3M^+ is greater than the sum of the abundances of Ph_2MET^+ and Ph_2MH^+ in Ph_3MET . This may indicate that the R_3M^+ ion is planar when charge delocalisation, and hence stability, will increase with the number of phenyl groups. For the compounds $\text{Et}_n\text{SnPh}_{4-n}$ ($n = 0-3$), PhSn^+ is the second or third most abundant ion, whereas tetraethyltin yields both SnH^+ and EtSn^+ in roughly equal abundance.

The tetraethyls show no Et_2M^+ ion but only the

One feature common to ethyl-Ge, -Sn, and -Pb compounds is methylene elimination giving ions of low abundance:—



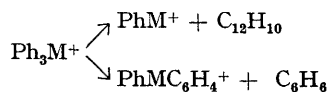
With Et_4Sn , at least, the ion $\text{C}_5\text{H}_{13}\text{Sn}^+$ (*i.e.*, $\text{Et}_2\text{SnCH}_3^+$) is probably not produced by methyl elimination followed by hydrogen attachment, since its abundance varies linearly with sample pressure. There was also no evidence for a vapour-phase rearrangement of Et_4Sn at 200°C before ionisation. The tin compound $\text{PhCH}_2\text{-CH}_2\text{-SnPh}_3$ also showed two low-abundance peaks ascribable to methylene or ethylene elimination.



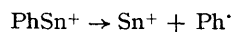
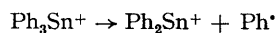
The ion MeGeH_2^+ may be formed by a similar process.



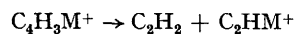
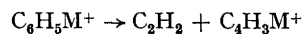
Phenyl-containing metal ions decompose by diverse routes. Metastable peaks corresponding to biphenyl and benzene elimination are observed.



Phenyl radical elimination is observed with tin,



Fragmentation of Ph-M⁺ ions is observed at 70eV, but not 20eV.



All phenyltin compounds show the ion C₄H₃Sn⁺ whilst the spectra of Ph₄Sn, EtSnPh₃, and Et₂SnPh₂ also produce ions C₁₀H₇Sn⁺ and C₈H₅Sn⁺. In contrast to alkyl compounds the arylgermanes Ph₄Ge and (*p*-MeC₆H₄)₄Ge lose one hydrogen atom to give both the singly and doubly charged ions *e.g.*, (Ph₃GeC₆H₄)⁺ and (Ph₃GeC₆H₄)²⁺.

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¹ A. Carrick and F. Glockling, *J. Chem. Soc. (A)*, 1966, 623; V. H. Dibeler and F. L. Mohler, *J. Res. Nat. Bur. Standards*, 1951, **47**, 337; E. I. Quinn, V. H. Dibeler, and F. L. Mohler, *ibid.*, 1956, **57**, 41; V. H. Dibeler, *ibid.*, 1952, **49**, 235.