

Studies in aryltin chemistry. Part 11. The effects of substituent type and position on the disintegration patterns in the mass spectra of Ar_4Sn and Ar_3SnX compounds¹

Jack M. Miller^{a,*}, Yongchong Luo^a, Ivor Wharf^b

^a Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada

^b Department of Chemistry and Chemical Technology, Dawson College, Westmount, Quebec H3Z 1A4, Canada

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Abstract

Complete EI and positive-ion FAB (matrix liquids: 2-nitrophenyl octyl ether (NPOE) and 3-nitrobenzyl alcohol (NBA)) mass spectra are reported for Ar_4Sn (Ar = *p*-Tol, *m*-Tol, 3,5-Xyl, *o*-Tol, *p*-FC₆H₄, *m*-FC₆H₄, 3,5-F₂C₆H₃, *p*-ClC₆H₄, 3,5-Cl₂C₆H₃, *p*-CF₃C₆H₄, and *m*-CF₃C₆H₄) and Ar_3SnX (Ar = Mes, X = Cl, Br, I; Ar = *o*-Tol, X = I). Comparison with phenyltin data shows methyl substituents produce little change in disintegration patterns except when in the *ortho*-position, in which case loss of ArH is promoted. Halogen substituents produce both **substituent type** and **position effects** in disintegration patterns. Differences are seen between EI and positive-ion FAB mass-spectra results which would indicate that for the latter, matrix mediated processes are more significant than gas-phase disintegration pathways. Negative-ion FAB mass spectra were observed for only a few of the compounds studied in this work.
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1. Introduction

The first mass spectrometric studies of phenyltin compounds appeared in 1966 [1,2] and these were then amplified by the definitive paper of Chambers et al. [3]. Reports of the mass spectra (MS) of fluorophenyltin derivatives soon followed [4–6] while several phenyltin systems with organic radicals or ligands of varying complexity attached have been characterized by mass spectrometry [7–9], as well as Ph_3SnMR_3 (M = Si, Ge, Sn) [10]. More recently, a surface ionization (SI) study of $(\text{C}_6\text{H}_5)_3\text{Sn}$ has appeared [11].

Our work began with an electron impact (EI) study of hexamethylphosphoramide (HMPA) adducts of Ph_3SnX and Ph_2SnX_2 (X = Cl, Br, I) [12]. As with all main group organometallics, particularly Group 14, parent molecular ion peaks (M^+) were found to be very

weak or non-existent and fast atom bombardment (FAB) mass spectra of the same HMPA adducts were measured [13] in the hope of alleviating this problem. The matrix liquids were HMPA or *p*-nitrophenyl octyl ether (NPOE). Although M^+ were still not observed, differences between EI and FAB spectra were ascribed to interactions between the matrix and the aryltin halide species. The role of NPOE in removing excess energy from ions before desorption from the matrix was also suggested.

The present paper is part of a series [14] concerned with the effects of phenyl ring substituents on the structures and spectroscopic and biological properties of aryltin compounds. Earlier, the effects of *p*-fluoro- and *p*-chloro-substituents on the EI and FAB (NPOE matrix) mass spectra of Ar_4Sn , Ar_3SnX (X = Cl, Br, I) and their HMPA adducts were reported [15]. As before, parent ions were absent in both EI and FAB spectra but halide migration to (and in some cases, exchange at) tin was observed leading to SnX^+ as a major species, although not in the FAB spectra of the HMPA adducts. In this study, we present the effects of various sub-

* Corresponding author. Tel.: +1 416 6885550 ext. 3402; Fax: +1 416 6882789 or 6829020.

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stituents (CH₃, CF₃, F, Cl) and ring positions (*o*-, *m*- or *p*-) in the EI and FAB mass spectra of Ar₄Sn together with detailed fragmentation data. We have also considered the effect of *o*-CH₃ groups on the spectra of various Ar₃SnX (X = Cl, Br, I).

2. Experimental details

The compounds examined in this work were prepared previously [16,17].

All positive/negative ion FAB, EI and their linked scan mass spectra were recorded on a Kratos Concept IS double focusing mass spectrometer using a combined EI/CI source and a modified Kratos FAB source. The samples were introduced by a heated solid probe for EI and an unheated probe for FAB. For collecting normal EI and EI linked scan mass spectra, an accelerating voltage of 8 kV was used with a corresponding mass range of 10 to 1000 mass units. When collecting positive/negative ion and positive ion linked scan FAB mass spectra, an accelerating voltage 6 kV was used. The resolving power used was 1000 throughout and the magnet was scanned at 10 s/decade for all spectra.

For electron impact mass analysis, the source was heated to 180°C. A 70 eV ionization energy was used for bombardment. Calibration of both normal and linked scan mass spectra was performed using perfluorokerosene (PFK).

For FAB analysis, samples which were dissolved in the matrix were bombarded on an unheated stainless steel probe tip with energetic fast atoms produced by Ion Tech. saddle-field type fast atom gun. Xenon was used to generate the bombarding atoms and the gun was operated at approximately 1.0 mA emission, providing fast atoms with an energy of 7.5 keV. Calibration was done using Tris-(perfluoroheptyl)-*S*-triazine for positive ion FAB while for negative ion FAB CsI was used.

For recording linked scan spectra, the electric (*E*) and the magnetic (*B*) fields were scanned in such a way that the value *B*/*E* (fragment ion scans), *B*²/*E* (precursor ion scans) and *B*²(1 - *E*)/*E*² (constant neutral loss scans) remained constant. Metastable transitions in the first field-free region were observed, i.e. in the region before the electrostatic analyzer but after the accelerating region of the ion source. For recording the collision activation positive ion FAB linked scan spectra, helium was used as the collision gas at a pressure sufficient to attenuate the main ion beam by 50% of its original value.

Data were collected with a Kratos DS-90 data system and transferred to a Sun SparcStation10 where all computations were carried out with a Kratos Mach 3 data system. Ions were further identified by pattern matching of isotope clusters, using deconvolution when necessary. For the FAB spectra, the data system was used for

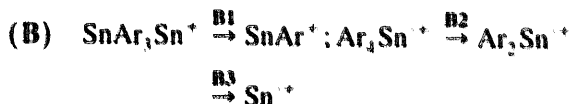
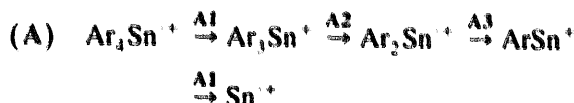
background subtraction of the matrix peaks. At low masses in particular for aryltin compounds, the matrix subtraction did not always completely remove the matrix peaks, a result of the variation of the matrix spectrum with concentration.

3. Results

3.1. EI Spectra

Electron impact data for Ar₄Sn studied in this work as well as for Ph₄Sn [3] and (*p*-YC₆H₄)Sn (Y = F, Cl) [15], and for (Mes)₃SnX and (*o*-Tol)₃SnI are presented in Tables 1 and 2, respectively. As in all previous EI spectra of aryltin compounds, 70–90% of the ion-current is carried by tin containing species which are listed in the tables. The most common organic ions are Ar₂⁺, (Ar + H)⁺, Ar⁺, (Ar₂-H)⁺, (Ar₂-F)⁺, and (Ar-F)⁺. For (x-CF₃C₆H₄)₃Sn (x = *m*, *p*), these peaks become quite intense and also include (Ar₂-2F)⁺, (Ar₂-2F-HF)⁺, (Ar + 2F)⁺, and (Ar-2F)⁺. Linked scan spectra were determined for all compounds reported in Tables 1 and 2. In many cases, species not detected in regular EI mass spectra were observed and the disintegration schemes to be presented outline the wealth of information available from the fragmentation pathways derived from these studies.²

The EI mass spectra of most Ar₄Sn (Table 1) like Ph₄Sn [3,15] show no molecular ion peaks, and are dominated by the species, Ar₃Sn⁺, Ar₂Sn⁺, Ar⁺, and Sn⁺, the first being predominant in all spectra. These ions can be formed either by sequential loss of Ar⁺ (A) or by loss of Ar₂ (B), with the favored processes being OE⁺ → EE⁺ and EE⁺ → EE⁺ [18].



These together give the general disintegration pathways shown in Scheme 1 for Ar₄Sn. However, not all of these processes are observed in fact. Thus, as in SnPh₄ [3], processes confirmed for most Ar₄Sn (————→) by linked scans were B1 (all systems), B2 and A4.³ The other processes involving loss of Ar⁺ are A1, which is essential to form Ar₃Sn⁺ but was confirmed only for

² Complete fragmentation patterns (EIMS) for all compounds studied in this work are available from the authors (J.M.M.).

³ The designation used is A, B etc. for the reaction followed by a number 1 etc. indicating which of the reactions in a series is being referred to.

Table 1
Mass-spectral data ^a (EI) for Ar₃Sn

Ion ⁺	Ar = Ph ^b	= <i>p</i> -Tol ^c	= <i>m</i> -Tol ^c	= 3,5-Xyl ^d	= <i>o</i> -Tol ^c
(M-H) ⁺	–	–	0.9	0.9	–
Ar ₃ Sn ⁺	49.8	49.2	47.1	25.9	58.7
Ar ₂ SnC ₇ H ₆ ⁺	–	–	–	1.2	–
Ar ₂ Sn ⁺	11.8	23.1	24.6	20.5	–
ArSnC ₇ H ₆ ⁺	–	–	–	1.0	11.1
ArSn ⁺	19.2	12.5	12.5	14.0	19.3
SnC ₇ H ⁺	–	–	–	7.5	–
SnC ₆ H ₃ ⁺	–	–	–	7.5	–
Sn ⁺	20.0	15.0	14.9	20.7	10.7
	Ar = <i>p</i> -FC ₆ H ₄ ^b	= <i>m</i> -FC ₆ H ₄	= 3,5-F ₂ C ₆ H ₃		
Ar ₃ Sn ⁺	51.0	28.4	34.8		
Ar ₂ Sn ⁺	3.9	2.6	2.1		
ArSn ⁺	17.6	19.7	19.8		
SnF ⁺	9.8	22.2	23.4		
Sn ⁺	17.2	27.1	19.8		
	Ar = <i>p</i> -ClC ₆ H ₄ ^b	= 3,5-Cl ₂ C ₆ H ₃			
(M-H) ⁺	–	1.9			
Ar ₃ Sn ⁺	52.5	35.1			
Ar ₂ SnCl ⁺	–	1.0			
Ar ₂ Sn ⁺	4.8	1.1			
ArSn ⁺	14.7	18.1			
SnCl ⁺	22.8	35.1			
Sn ⁺	5.2	7.0			
	Ar = <i>p</i> -CF ₃ C ₆ H ₄	= <i>m</i> -CF ₃ C ₆ H ₄			
Ar ₃ SnC ₇ H ₃ F ₃ ⁺	3.6	4.1			
Ar ₃ Sn ⁺	68.5	55.3			
Ar ₂ SnF ⁺	2.4	3.3			
Ar ₂ Sn ⁺	1.2	1.8			
ArSn ⁺	16.1	20.4			
SnC ₇ H ₃ F ₃ ⁺	–	4.0			
SnF ⁺	5.0	7.7			
Sn ⁺	3.3	3.4			

^a Percentage (≥ 1) of the total positive ion current carried by tin containing ions.

^b Ref. [15].

^c Tol = CH₃C₆H₄.

^d Xyl = (CH₃)₂C₆H₃.

Table 2
Mass-spectral data (EI) for Ar₃SnX

Ion ⁺	X = Cl		X = Br		X = I		
	Ar = Ph ^b	= Mes ^c	= Ph ^b	= Mes ^c	= Ph ^b	= <i>o</i> -Tol ^d	= Mes ^c
Ar ₃ Sn ⁺	2.8	2.0	18.0	3.1	59.7	59.2	62.1
Ar ₂ SnX ⁺	50.9	–	30.8	–	3.4	6.4	–
Ar(C ₉ H ₁₀)SnX ⁺	–	40.4	–	39.7	–	–	–
Ar(C ₈ H ₇)SnX ⁺	–	6.2	–	3.9	–	–	–
Ar ₂ Sn ⁺	0.8	–	2.4	–	0.8	–	–
ArSn(Ar-H) ⁺	–	4.7	–	4.7	–	3.0	13.2
ArSnX ⁺	3.4	–	2.6	–	–	–	–
Sn(Ar-H)X ⁺	–	2.9	–	2.4	–	1.9	–
ArSn ⁺	11.6	21.8	19.5	19.2	20.9	18.3	18.0
SnX ⁺	24.7	10.6	20.0	12.6	4.8	4.5	–
Sn ⁺	5.7	10.3	6.3	11.4	10.3	6.8	6.7

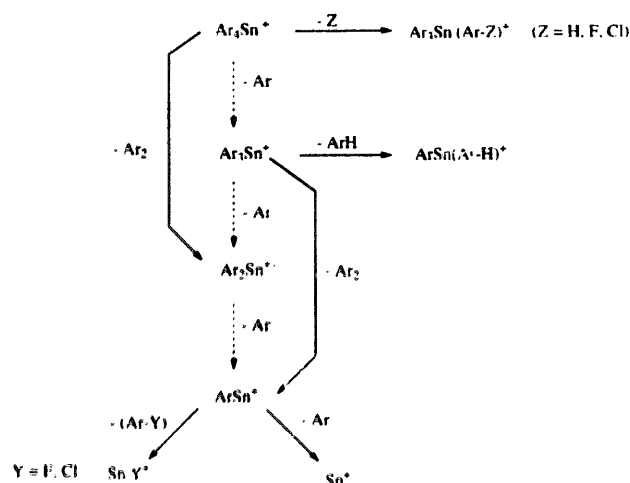
^a Percentage (≥ 1) of the total positive ion current carried by tin-containing ions.

^b Ref. [15].

^c Mes = 2,4,6-(CH₃)₃C₆H₂.

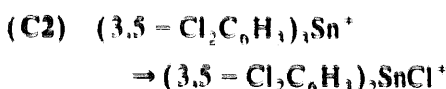
^d *o*-Tol = *o*-CH₃C₆H₄.

Ar_4Sn : Ar = Ph; *m*-Tol; *p*-Tol; 3,5-Xyl; *m*-FC₆H₄; 3,5-X₂C₆H₃ (X = F, Cl)

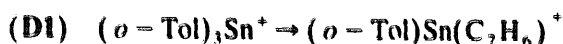


Scheme 1. Ar_4Sn (Ar = Ph, *p*-Tol, *m*-Tol, 3,5-Xyl, *m*-FC₆H₄, 3,5-X₂C₆H₃ (Y = F, Cl)).

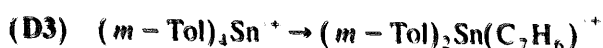
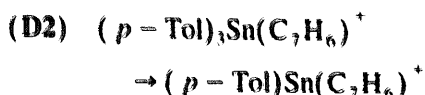
the halophenyl systems (---→), and **A2** and **A3** which were observed in only in Ar = *p*-Tol and 3,5-Xyl, and Ar = 3,5-Xyl respectively (···→) and thus are very minor contributors to the overall disintegration process for Ar_4Sn . Process **B3**, which was earlier confirmed for SnPh_4 [3], was not verified by linked scanning in any fragmentation patterns in this work and is thus omitted from Scheme 1. The halophenyl systems studied here all form SnY^+ ions as confirmed by the observed halide migrations (C).



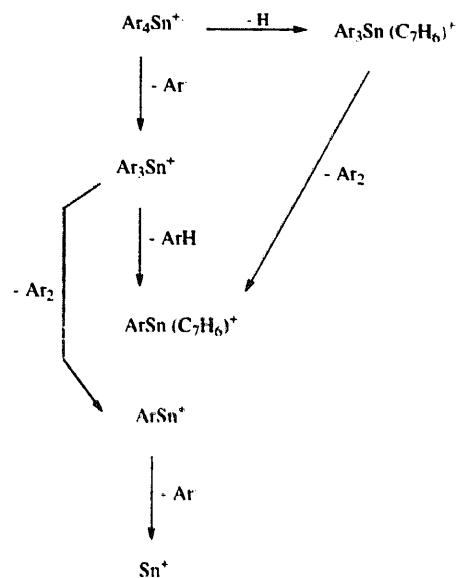
While EIMS data for (*p*-Tol)₄Sn and (*m*-Tol)₄Sn differ only slightly from those for Ph₄Sn, a significant **position effect** is shown in the EIMS for (*o*-Tol)₄Sn (Scheme 2) where all processes have been confirmed by linked scans. Here the clearly favored path for decomposition of M^+ is **A1** while *o*-CH₃ groups facilitate loss of toluene from Ar_3Sn^+ , to give an EE^+ (**D1**). This is a typical 'ortho-effect' [18].



Process **D1** may also be favored by the formation of a stable benzylium or tropylium type ion, and this effect might also account for similar processes confirmed for *p*- or *n*-tolyl systems in Scheme 1 as well as **D2** and **D3** even if OE^+ species are involved.

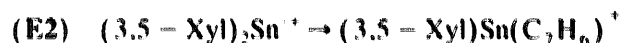


(*o*-Tol)₄Sn



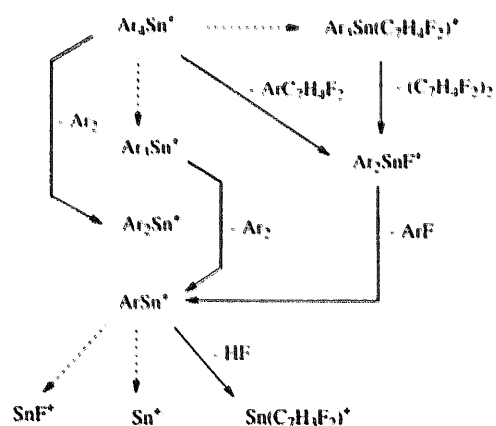
Scheme 2. (*o*-Tol)₄Sn.

In the same way, loss of methyl from 3,5-xylyl (C₈H₆) compounds (**E**) will produce both EE^+ and OE^+ species containing C₇H₆ although only process **E3** was actually confirmed in elucidating the fragmentation pattern of (3,5-Xyl)₄Sn.



Halophenyltin compounds show both **substituent type** and **position effects**. Thus, the EIMS of both *para*- and *meta*-substituted Ar_4Sn have much decreased Ar_2Sn^+ intensities when compared with the archetypal Ph₄Sn mass-spectrum, but when we compared the (*p*-YC₆H₄)₄Sn and (*m*-YC₆H₄)₄Sn EIMS, the latter has both much reduced Ar_3Sn^+ and increased SnX^+ . The

(*p/m*-CF₃C₆H₄)₄Sn



Scheme 3. (*p/m*-CF₃C₆H₄)₄Sn.

Table 3
Mass-spectral data ^a (positive-ion FAB ^b) for Ar₃Sn

Ion ⁺	Ar = Ph ^c		= <i>p</i> -Tol ^d		= <i>m</i> -Tol ^d		= <i>o</i> -Tol ^d	
	NPOE	NBA	NPOE	NBA	NPOE	NBA	NPOE	NBA
Ar ₃ Sn(Mat ^e) ⁺	3.1	2.1	2.1	2.1	4.4	2.3	–	–
(M–H) ⁺	–	–	0.7	–	3.4	1.5	(1.5) ^g	–
Ar ₃ SnCH ₃ ⁺	–	1.9	–	–	2.4	2.1	–	–
Ar ₃ Sn ⁺	55.0	68.2	81.6	81.6	48.7	53.6	36.3	73.9
Ar ₂ Sn(C ₆ H ₄) ⁺	–	–	–	–	1.2	–	–	–
Ar ₂ SnOH ⁺	–	–	–	–	3.6	2.9	–	–
Ar ₂ SnCH ₃ ⁺	–	2.6	–	–	–	–	–	–
Ar ₂ Sn ⁺	2.5	–	–	–	–	–	–	–
ArSnC ₇ H ₆ ⁺	–	7.1	(1.1) ^f	–	5.5	5.9	–	–
ArSn ⁺	16.1	18.2	14.6	14.6	17.7	17.5	10.6	15.0
Sn ⁺	23.2	–	–	–	12.6	14.3	51.5	11.1

	Ar = <i>p</i> -CF ₃ C ₆ H ₄		= <i>m</i> -CF ₃ C ₆ H ₄	
	NPOE	NBA	NPOE	NBA
Ar ₃ Sn(Mat) ⁺	10.0	5.3	8.2	5.5
Ar ₃ SnC ₇ H ₄ F ₂ ⁺	3.3	1.5	1.1	4.0
Ar ₃ Sn(H ₃ F) ⁺	–	8.0	–	4.3
Ar ₃ Sn ⁺	51.7	39.6	73.1	54.9
Ar ₂ SnC ₇ H ₄ F ₂ ⁺	5.3	2.4	–	2.7
Ar ₂ SnC ₆ H ₄ ⁺	2.0	1.4	–	1.1
ArSn(C ₇ H ₄ F ₂) ⁺	–	3.0	–	4.0
ArSn(C ₇ H ₄ F ₂) ⁺	1.6	–	–	–
ArSn(C ₇ H ₄ F ₂) ⁺	–	0.6	–	2.9
ArSn ⁺	22.7	17.3	17.6	20.6
SnF ⁺	–	11.3	–	–
Sn ⁺	3.4	9.6	–	–

^a Percentage (≥ 1) of the total positive current carried by tin-containing ions.

^b Matrix liquids, 4-nitrophenyl octyl ether (NPOE), and 3-nitrobenzyl alcohol (NBA).

^c Ref. [15].

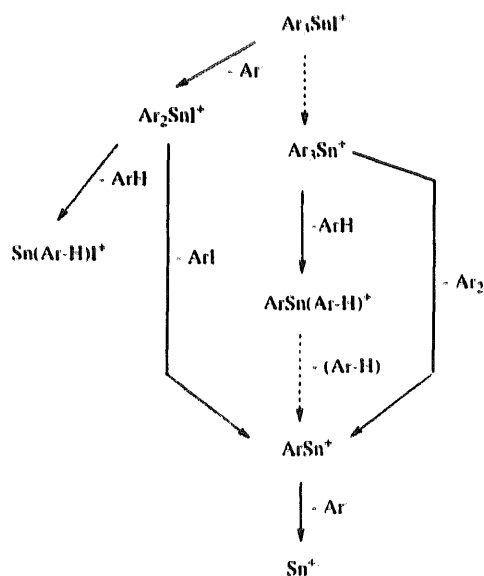
^d Tol = 2,4,6-CH₃C₆H₃.

^e Mat = NPOE or NBA.

^f ArSn(C₇H₄)⁺.

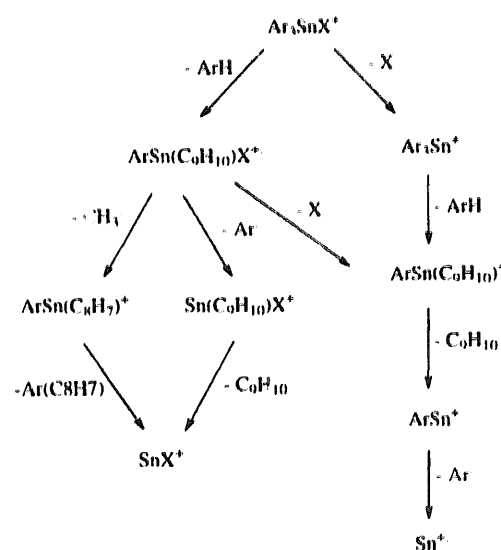
^g (M + 2H)⁺.

Ar₃SnI: Ar = *o*-Tol; Mes.



Scheme 4. Ar₃SnI (Ar = *o*-Tol, Mes).

(Mes)₃SnX: X = Cl; Br



Scheme 5. (Mes)₃SnX (X = Cl, Br).

spectra are almost the same with either one or two *meta*-substituents. In contrast, the spectra of (*p*-CF₃C₆H₄)₄Sn and (*m*-CF₃C₆H₄)₄Sn are very similar, i.e., there is no position effect but comparison with EIMS for (*p*-Tol)₄Sn and (*m*-Tol)₄Sn show a strong substituent type effect, with much more Ar₃Sn⁺ and much smaller amounts of Ar₂Sn⁺ being observed. No processes corresponding to loss of Ar[·] (A1–4) or formation of SnF⁺ by fluorine transfer were confirmed by linked scans, but some of these must occur (---→) in the disintegration (Scheme 3) for these compounds as the resulting ions are observed.

The observation of an 'ortho-effect' in the EIMS of (*o*-Tol)₄Sn then prompted a study of (*o*-Tol)₃SnI and (Mes)₃SnX for comparison with our previous data for Ph₃SnX (Table 2). Results for (*o*-Tol)₃SnI and Ph₃SnI are essentially the same with loss of I[·] or Ar[·] from the molecular ion, giving Ar₃Sn⁺ or Ar₂SnI⁺. The former process predominates, presumably because of the weak

Sn–I bond as suggested by Chambers et al. [3]. However, in the *o*-tolyl case, Ar₂SnI⁺ or Ar₃Sn⁺ can then lose toluene to form benzylium (or tropylium) type species, but the major process appears to be loss of ArI or Ar₂ to yield ArSn⁺ (Scheme 4). In the case of the mesityltin analog, the weaker Sn–I bond, compared with that of Ph₃SnI [19], causes loss of I[·] from M⁺ to give (Mes)₃Sn⁺ to be the sole disintegration process. The (Mes)SnC₉H₁₀⁺ ion, however, forms (Mes)Sn⁺ directly (···>), as confirmed by linked scan analysis. The much greater tin–halogen bond strength means this pathway is a very minor one for (Mes)₃SnX (X = Cl, Br) (Scheme 5). Instead, the Sn–X bond is preserved when the molecular ion loses mesitylene (not mesityl) to form the OF⁺, (Mes)Sn(C₆H₁₀)X⁺, in surprisingly high abundance. This then loses X[·] or Mes[·] to form EE⁺ species and even CH₃ to form (Mes)Sn(C₈H₇)X⁺, which again may include a benzylium or tropylium moiety.

Table 4
Mass-spectral data ^a (Positive ion FAB ^b)

Ion ⁺	Ar = <i>m</i> -FC ₆ H ₄	= 3,5-F ₂ C ₆ H ₃	= 3,5-Cl ₂ C ₆ H ₃
(a) Ar₄Sn			
Ar ₃ Sn · NBA ^c	4.5	6.2	10.2
Ar ₃ Sn · OCH ₂	7.1	–	–
Ar ₃ Sn · OCH ^d	–	–	1.6
Ar ₃ Sn ⁺	43.5	48.1	61.5
Ar ₂ SnC ₉ H ₁₀ Cl ⁺	–	–	3.2
Ar ₂ SnCl	–	–	0.9
ArSn ⁺	28.2	20.3	22.7
SnF ⁺	–	14.4	–
Sn ⁺	16.7	11.0	7.1
(b) Ar₃SnX⁺			
	Ar = Mes ^d		<i>o</i> = Tol ^e
	X = Cl ^f	= Br ^g	= I ^h
(M–H) ⁺	4.5	2.8	–
Ar ₃ Sn · HNO ₂	–	–	6.1
Ar ₃ Sn ⁺	27.9	20.8	35.3
Ar ₂ SnX ⁺	–	–	18.9
ArSn(C ₉ H ₁₀)X ⁺	–	17.6	–
Ar ₂ SnCH ₃ ⁺	–	2.5	–
ArSn(Ar–H) ⁺	4.1	5.0	7.6
Sn(Ar–H)X ⁺	2.3	1.5	–
ArSnCH ₂	1.8	2.6	3.0
ArSn ⁺	23.6	18.9	28.0
SnX ⁺	6.8	4.7	–
SnCH ₃ ⁺	10.9	10.3	–
Sn ⁺	10.0	8.2	16.0

^a Percentage (≥ 1) of the total positive ion current carried by tin-containing ions.

^b Matrix liquid, 3-nitrobenzylalcohol (NBA).

^c The more significant ions given in the table.

^d Mes/2,4,6-(CH₃)₂C₆H₂; ^e *o*-Tol/*o*-CH₃C₆H₄.

^f Add: Ar₃Sn · CH₃⁺, 1.0; Ar₂SnX · CH₂, 2.9; Ar(C₈H₇)SnX⁺, 3.1%.

^g Add: Ar₃Sn · CH₃⁺, 1.5; Ar₂SnX · CH₂, 1.9; ArSn(C₈H₆)⁺, 1.2%.

^h Add: Ar₃Sn · NBA · H₂O, 0.7; Ar₃Sn · CH₃, 3.2%.

ⁱ Add: Ar₃Sn · NBA⁺, 0.7; Ar₂SnI · NBA⁺, 0.6; M⁺, 0.6; Ar₃SnC₆H₄⁺, 1.8%.

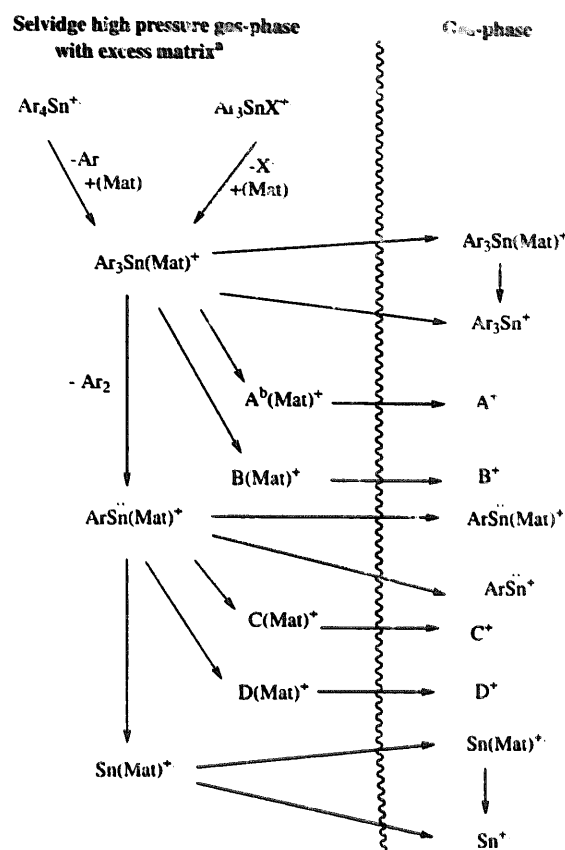
3.2. Positive ion FAB spectra

As in an earlier study of group 14(IV) organometallic halides [20], several matrix liquids were tried, including glycerol, monothioglycerol, sulfolane, 2,2'-thiodiethanol, diamylphenol, as well as 2-nitrophenyl octyl ether (NPOE) and 3-nitrobenzyl alcohol (NBA). Only the latter pair provided usable spectra, with the last one (NBA) giving the best results for the aryltin compounds studied in this project. A comparison of NPOE and NBA data for several Ar_4Sn is shown in Table 3, while NBA data alone are given in Table 4.

Positive-ion FABMS, especially the very detailed fragmentation patterns determined by linked scans analyses,⁴ imply different, presumably matrix-mediated disintegration processes which occur instead of those in EI spectra. Thus, in our Ar_4Sn spectra, the major species are Ar_3Sn^+ followed by ArSn^+ , with some $\text{Ar}_3\text{Sn}(\text{Mat})^+$ ($\text{Mat} = \text{NPOE}$ or NBA). However, no Ar_2Sn^+ is observed. We, therefore, suggest loss of Ar from the molecular ion is assisted by the matrix, presumably in the high pressure selvidge region, which then stabilizes the EE^+ ions by adduct formation (Scheme 6). This then loses Ar_2 and then Ar in the selvidge high pressure region above the sample or in the gas phase, or collisional processes cause partial fragmentation of the adduct ions. The energy lost by collision in the high pressure region gives ions of lower internal energy, and thus, after loss of a molecule of coordinated matrix, gives the species observed which appear not to disintegrate further. This is shown by the very simple (*o*-Tol)₄Sn FABMS spectra. Thus the following fragmentations are observed under collisional activation (CA) conditions, suggesting structures quite different from those observed in the EI spectrum.



It is interesting that the fragmentation from the Ar_3Sn^+ ion itself under linked scan conditions can be very complex — much more so than that observed in the EI spectra. These include fragmentation of the aromatic substituents, hydride transfer to tin, losses of additional hydrogen atoms etc. There is also evidence for a one-step formation of tin ions from the triaryl-tin ions. For systems containing a CF_3 group, there is evidence for fluorine migrations. SnF^+ is observed and there is also evidence for HF loss and HF adduct



Scheme 6. Skeletal disintegration scheme (positive-ion FABMS) for Ar_4Sn and Ar_3SnX .

formation. However, these complex reactions occur in the collision cell, removed from the high pressure selvidge, dominated by matrix molecules, ions and radicals.

Differences are seen between the EI and FAB mass spectra of Ar_3SnX ; e.g., larger amounts of ArSn^+ in all cases in FAB. There is less Ar_3Sn^+ seen in the FAB spectra, when $\text{X} = \text{I}$, but more when $\text{X} = \text{Cl}$ or Br , compared to the EI data. This is indicative of the relatively constant abundance of this species in FAB as X is changed from Cl to Br to I , compared to the EI data for which there is more than an order of magnitude variation. This behavior indicates matrix mediated processes are significant here, whether in solution, or in the high pressure region above the sample.

3.3. Negative ion FAB spectra

The negative ion spectra of these compounds in NBA were very much weaker in overall intensity than the positive ion FAB or EI spectra, limiting the compounds for which reliable data could be obtained to those listed in Table 5. With low absolute intensities, reliable linked scan data could not be obtained and we

⁴ Complete fragmentation patterns (+ve ion FABMS) for all compounds studied in this work are available from the authors (J.M.M.).

Table 5
Negative ion FAB mass-spectral data^a of aryltin compounds in NBA matrix

Ion ⁻	Ar = <i>m</i> -CF ₃ C ₆ H ₄	= <i>p</i> -CF ₃ C ₆ H ₄	
(a) (x-CF ₃ C ₆ H ₄) ₄ Sn (x = <i>m</i> , <i>p</i>)			
(M · NBA + H) ⁻	–	26.6	
M · NBA ⁻	23.0	–	
M · NO ₂ ⁻	6.8	8.3	
M · CH ₃ ⁻	9.2	12.7	
M ⁻	2.2	2.2	
(Ar ₃ SnF ₂) ⁻	3.0	0.5	
Ar ₃ Sn · O ⁻	6.9	8.7	
Ar ₃ Sn ⁻	22.2	41.1	
Ar ₂ Sn · F ⁻	14.0	15.2	
Ar ₂ Sn ⁻	3.9	4.8	
ArSnO ⁻	4.1	4.0	
ArSn ⁻	4.7	2.6	
(b) (3,5-X ₂ C ₆ H ₃) ₄ Sn (X = F, Cl, CH ₃)			
	Ar = 3,5-F ₂ C ₆ H ₃	= 3,5-Cl ₂ C ₆ H ₃	= 3,5-(CH ₃) ₂ C ₆ H ₃
(M · NBA-H) ⁻	14.1	–	–
(M · NBA-2H) ⁻	–	27.6	–
(M · NBA-3H) ⁻	–	–	9.4
(Ar ₃ Sn · NBA-NO ₂ -H ₂ O-3H) ⁻	10.9	–	–
M · NO ₂ ⁻	4.4	–	–
(M · NO ₂ -2H) ⁻	–	9.9	–
M · CH ₃ ⁻	–	–	14.3
M ⁻	5.2	3.1	1.1
(M-C ₆ H ₅) ⁻	–	7.0	–
Ar ₃ SnF · C ₆ H ₅ ⁻	–	7.7	–
Ar ₃ SnF ⁻	6.5	–	–
Ar ₃ Sn · CH ₂ ⁻	–	4.8	2.3
Ar ₃ Sn ⁻	24.1	23.6	44.1
Ar ₂ SnX ⁻	11.1	11.5	8.2
Ar ₂ Sn ⁻	8.1	3.0	12.9
(Ar ₂ Sn=C ₆ H ₄) ⁻	–	5.1	–
(ArSn=2F) ⁻	7.9	–	–
ArSn ⁻	–	–	11.0
(c) (2,4,6-(CH ₃) ₃ C ₆ H ₂) ₃ SnX (X = Cl, O ₂ CCH ₃)			
	X = Cl	O ₂ CCH ₃	
(M · NBA-NO ₂ -C ₇ H ₁₃) ⁻	–	8.6	
(Ar ₃ Sn · NO ₂ -CH ₃) ⁻	–	25.8	
(Ar ₂ SnX · NBA + NO ₂) ⁻	6.9	–	
Ar ₂ SnX ⁻	57.7	5.5	
Ar ₂ SnH ₂ · H ₂ O ⁻	–	9.4	
CH ₂ Sn · NBA	24.8	–	
(Ar ₂ Sn=H) ⁻	–	4.5	
ArSnCH ₃ ⁻	–	18.7	
ArSn ⁻	–	13.5	
Sn ⁻	10.5	14.9	

^a Percentage of the total negative ion current carried by tin-containing ions.

For (*o*-CH₃C₆H₄)₃SnI, the only significant ion is Ar₂SnI⁻.

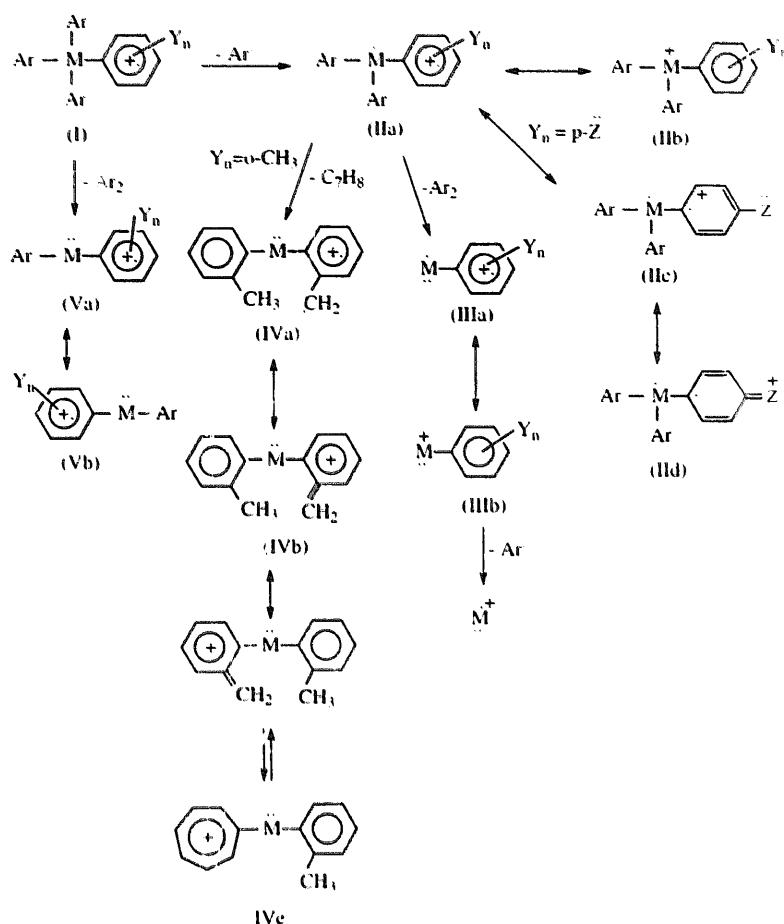
do not postulate any detailed fragmentation schemes for the negative ion data.

NBA related adduct ions are common in the negative ion spectra, and for those species with a halogen on the aromatic ring or side chain, the molecular anion is observed, unusual for compounds of tin. Not only are matrix adducts observed, but the nitro group from the NBA matrix is seen adducted to various tin-containing ions including the molecular anion. Ar₃Sn⁻ ions or

their adducts are seen for the tetra-aryl derivatives, while for the triaryl tin halides Ar₂SnX⁻ ions are much more abundant. Sn–O-containing ions are also more common than for the positive ion spectra.

4. Discussion

In discussions of molecular ion formation, it is generally assumed [18] that the electron lost is one of those



Scheme 7. Proposed structures of EIMS aryl-group 14 ions.

with the lowest ionization energy. For Ar_3M^+ ($\text{M} = \text{C} - \text{Pb}$), these are electrons occupying π -ring orbitals [21]. The resulting Ar_3M^+ Scheme 7 (I) can then lose Ar to form Ar_2M^+ which is also readily obtained by loss of I^- from Ar_3MI^+ . Although Ar_3M^+ (IIIa) may be planar (IIIb), like the structure of Ph_3C^+ , the metal-ring π -interaction implied in this case may be unlikely in the ground state [22]. However for $(\text{Mes})_3\text{Sn}^+$, agostic interactions between methyl group C-H bonds and the empty $5p_z$ orbital may well favor a planar geometry as indeed is found for the iso-electronic molecular species $(\text{Mes})_3\text{M}$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) [23–25]. Thus Ar_3M^+ species may be resonance hybrids of planar (IIIb) and non-planar (IIIa) forms with significant non-bonding electron density on M. However, spin-pairing would still be favored by the ring unpaired electron being at the *ipso*-carbon (IIIc) and stabilization of this resonance form by a π -donor substituent (IIId) would then account for the greater abundance of $(p\text{-ZC}_6\text{H}_4)_3\text{Sn}^+$ ($\text{Z} = \text{F}, \text{Cl}$) when compared with that of the *meta*-analog. If, however, we look at semi-empirical PM3 calculations (MacSpartan, Wavefunction, 1997) for these ions, the $\text{Sn}-\text{C}_3$ core is planar, with the rings rotated out of this plane propeller fashion in the case of *ortho*-substituents, and almost coplanar when the substituents are *meta*- or

para-. In addition, the tin computes to have a Mulliken charge of greater than plus one.

Loss of Ar_2 from Ar_3Sn^+ is the primary mode of formation of ArSn^+ (IIIa) which then loses Ar (IIIb) to give Sn^+ . With halogen substituents, SnZ^+ is formed as well. Earlier [15], it was suggested that halogen migration from the *para*-position went through a π -bonded (η^1 or η^6) intermediate. For *m*-Z migration, the π -intermediate need only have η^1 -coordination to tin with presumably less distortion of tin-aryl and tin-halogen bonds in this case accounting for the greater prevalence of SnZ^+ . We note also the increased halogen transfer with chlorine as a ring substituent. With CF_3 as a substituent, much less SnF^+ is observed again because of the much greater distortion in the π -bonded intermediate required for the appreciable tin-fluorine interaction which is necessary for the migration to occur.

With *o*- CH_3 groups present, loss of ArH competes with loss of Ar_2 from Ar_3Sn^+ , and indeed in $(\text{Mes})_3\text{SnX}$ ($\text{X} = \text{Cl}, \text{Br}$) is preferred to loss of Ar^- from the molecular ion even though an OE^+ is produced in this case. For the EE^+ , $\text{ArSn}(\text{Ar}-\text{H})^+$ ions (IVa), the positive charge is stabilized by resonance with benzylium species (IVb) which may equilibrate with the tropylium tau-

toomer (IVe). Formation of these ions by loss of CH_3 followed by hydrogen migration, will also account for the more complex EIMS noted for $(3,5\text{-Xyl})_4\text{Sn}$.

The EIMS data for Ar_4Sn ($\text{Ar} = \text{Ph}, o\text{-}, m\text{-}, p\text{-Tol}$) are similar to those reported many years ago for their germanium analogs [26], having Ar_3Ge^+ as the most abundant species. However, significant amounts ($> 1\%$) of species involving fragmentation of aryl groups attached to germanium are observed, but little or no Ge^+ , which is consistent with stronger $\text{Ge}-\text{C}$ compared with $\text{Sn}-\text{C}$ bonds. In contrast, Ph_4Pb has a very simple fragmentation pattern (3), the standard pathway being $\text{Ph}_4\text{Pb}^+ \rightarrow \text{Ph}_3\text{Pb}^+ \rightarrow \text{PhPb}^+ \rightarrow \text{Pb}^+$.

The most distinctive feature of the EIMS of Ar_4M ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) is the formation of the OE^+ , Ar_2M^+ . Indeed for Ph_4Si [27], the sequence, $\text{Ph}_4\text{Si}^+ \rightarrow \text{Ph}_2\text{Si}^+ \rightarrow \text{PhSi}^+$, is the preferred disintegration process, it had been suggested that a cyclic sigma-bonded structure was responsible for the apparent stability of Ph_2Si^+ . Instead, we propose that delocalization of the unpaired electron over both rings ($\text{Va} \leftrightarrow \text{Vb}$) may be sufficient to stabilize Ar_2M^+ species, in the same way as the classical EE^+ ions ($\text{IVa} \leftrightarrow \text{IVb}$). The analogy is striking. However, the possibility of π -bonded resonance forms analogous to that of Cp_2Sn [28] cannot be ruled out. Likewise ArM^+ may have a p -bonded structure similar to that of CpSn^+ [29] as well as the σ -bonded forms ($\text{IIIa} \leftrightarrow \text{b}$) shown in Scheme 7.

In the FAB spectra similar structures are likely, although some of the simplification that is observed, arises from the possibility that ions formed containing one or more coordinated matrix molecules may lack the empty low-lying orbitals required for some of the suggested rearrangements. With these pathways blocked other structures may dominate resulting in differing CA spectra from the same nominal mass ions in EI and FAB spectra.

In conclusion, these compounds offer some interesting insights into the influences of structural changes on the ion chemistry of tin.

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