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Negative Ion Mass Spectrometry of Organotin Compounds—An Aid to Environmental Monitoring?

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Positive-ion mass spectra of organotin compounds include a large number of different ions and therefore the absolute detection level is reduced. Negative-ion mass spectra are usually less complex and detection levels may therefore be improved. The negative-ion mass spectra of selected organotin compounds of the type R_4Sn, R_3SnCl, R_2SnCl_2 and $RSnCl_3$ were investigated using conventional electron impact ionization conditions. Simplified mass spectra, suitable for compound speciation, were obtained for R_3SnCl and R_2SnCl_2 materials but the same fragmentation product $SnCl_3^-$ was obtained from all the $RSnCl_3$ samples. R_4Sn compounds produced no negative-ion data in these studies. No significant gains in detection levels were noted but some interesting re-arrangement reactions leading to the formation of compounds consisting of substituents from the original tin atom were identified. These reactions may be of synthetic importance.

Keywords: negative ion MS; organotin; analysis; synthesis

INTRODUCTION

Conventional positive-ion electron impact (EI) mass spectra of organotin compounds of general formula R_nSX_{4-n} do not show significant molecular ions,[1-3] and where $n = 4$ for R = Me, Et, Pr and Bu the mass spectra exhibit a trend (see Table 1) towards structurally insignificant ions of low mass related to the alkyl substituent. This combination of low relative abundance of ions containing the central tin atom from a particular analyte in combination with the large number of tin isotopes renders positive-ion electron impact mass spectrometry a less sensitive detection method than if all the ionization were concentrated in a single significant species, the molecular ion for example.

The negative-ion mass spectra of a range of organotin compounds were therefore investigated to determine whether:

(1) the total ion signal was concentrated into a smaller range of ions;
(2) more significant molecular ion data were available;

Table 1 Comparison of the relative abundances of the major peaks in the mass spectra of compounds of the type R_4Sn[a]

R	RMM	R_3Sn^+	R_2Sn^+H	R_2Sn^+	RSn^+H_2	RSn^+	Sn^+H	R^+	Other ions
Methyl	180	100 (165)[b]	—	25 (150)	—	35 (135)	7 (121)	10 (15)	—
Ethyl	236	100 (207)	95 (179)	—	50 (151)	90 (149)	45 (121)	23 (29)	
n-Propyl	292	82 (249)	100 (207)	—	90 (165)	83 (163)	30 (121)	10 (43)	20 (41)
n-Butyl	348	40 (291)	65 (235)	—	100 (179)	—	50 (121)	30 (57)	43 (41)
t-Butyl	348	12 (291)	20 (235)	—	30 (179)	—	15 (121)	100 (57)	55 (41)

[a] These data show that the most abundant ions in the mass spectra exhibit a shift down and from left to right of the Table, indicating a move to more intense ions of structurally less significant data, particularly with respect to the central tin atom.
[b] The number in parentheses is the m/z value for the ion of the relative intensity cited.

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(3) potentially lower detection levels might be achieved.

Compounds covering the full range within the general formula R_nSnX_{4-n} were examined, where n ranged from 1 to 4 and the alkyl substitution varied between methyl and n-octyl (Oct) with the inclusion of a range of phenyl (Ph) derivatives. No mixed-substituent organic derivatives were studied, as can be seen from the summary in Table 2.

Table 2 Summary of the suppliers and the compounds used in this investigation[a]

	Compound type			
R	$RSnCl_3$	R_2SnCl_2	R_3SnCl	R_4Sn
Methyl	A	AL	V	AL
Ethyl	AL	V	AL	AL
n-Propyl	—	—	A	S
n-Butyl	AL	AL	AL	AL
t-Butyl	—	—	—	F
Cyclohexyl	—	—	AL	—
Phenyl	AL	AL	AL	—
Octyl	Sy	Sy	—	—
Dodecyl	Sy	Sy	—	—

[a] Abbreviations: A, Alfa; AL, Aldrich; F, Fluka; S, Strem; V, Ventron; Sy, synthesized. All chemicals were more than 93% pure.

THEORY

With modern mass spectrometers, changes in ion source polarity, detector voltage and (if appropriate) the magnet current can all be achieved within a matter of minutes and negative ions can be studied almost as readily (Eqs [1–3]) as the positive species.[4]

The formation of negative ions in a conventional EI ion source can occur as follows:[5]

$$AB + e^- \rightarrow AB^- \quad \text{(associative resonance capture)} \qquad [1]$$

$$AB + e^- \rightarrow A^- + B \quad \text{(dissociative resonance capture)} \qquad [2]$$

$$AB + e^- \rightarrow A^+ + B^- + e^- \quad \text{(ion-pair production)} \qquad [3]$$

Resonance capture occurs at relatively high ion source pressures; the dissociative reaction has been cited as the mechanism leading to the formation of the Cl^- ion.[6] Ion-pair production and dissociative resonance capture both occur over the 0–15 eV ion energy range and should therefore be the principal mechanisms leading to the formation of any observed ions. Samples containing halogens have been observed to produce the halide anion which then undergoes a nucleophilic addition to a neutral molecule leading either to an adduct ion or to a displacement reaction.[7] The *d*-orbitals from the tin atom may be involved in charge stabilization.

EXPERIMENTAL

Authentic samples of the organotin compounds specified in Table 2 were introduced into the mass spectrometer using the direct insertion probe. The samples were volatilized from the probe tip and mass spectra were recorded under conventional 70 eV electron impact conditions, but selecting negative ions. The indicated pressures within the ion source were maintained below 5×10^{-6} torr.

Instrument	VG TRIO 3
Mass spectrometer	Q1 only operating
Scan rate	m/z 40–500 in 1 s
Resolution	>1000
Mode	Negative ion

RESULTS

Each separate fragment ion is represented by a group of peaks derived from the isotope of each of the constituent elements (six from tin and two from chlorine). In order to simplify the approach, therefore, the mass spectral data are discussed in terms of the peaks relating to the principal isotopes (^{120}Sn and ^{35}Cl) and the appropriate fragment ions. The mass spectral data, m/z values and relative abundances, for those compounds where the data are not readily available, are cited in Tables 3, 4 and 5.

The results suggest that chemical ionization conditions were present in the ion source whereas the indicated pressures were low. Deliberate chemical ionization conditions using both methane and ammonia revealed that the Cl products were *not* the same as those observed in the current series of experiments.

$RSnCl_3$ compounds

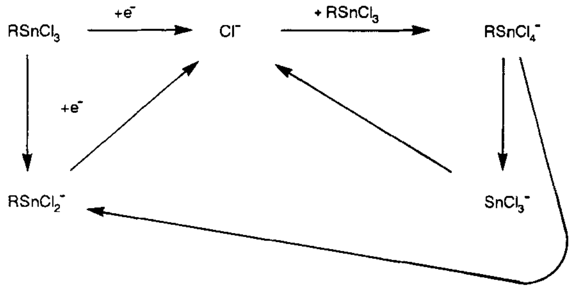
The mass spectra of these compounds are dominated by the effect of the three chlorine atoms, with the $SnCl_3^-$ and Cl^- anions being the most abundant species produced. The only other fragment ions (Table 3) observed were derived from the loss of a chlorine atom to produce the $RSnCl_2^-$ anion, whilst the species derived from the nucleophilic attack of a Cl^- anion on a neutral organotin molecule, i.e. $RSnCl_3Cl^-$, was observed, albeit at low abundance for all the compounds investigated. This type of reaction has been reported in negative chemical ionization studies where high pressures are utilized, but in this current work conventional ion source pressures, consistent with EI systems, were maintained. The ionization/fragmentation pathway is unclear; at least two possible routes are shown in Scheme 1. In parallel with the results from the positive-ion studies, the phenyl derivative showed different fragmentation processes. In this case the ion resulting from the loss of chlorine, $PhSnCl_2^-$ (*m/z* 267) had a relative abundance (RA) of 96% compared with a maximum value of 20% for the similar alkyl derivatives.

Table 3 Summary of the relative abundance of the major fragments from the negative-ion mass spectra of $RSnCl_3$ compounds

R	RMM[a]	$SnCl_3^-$	Cl^-	$RSnCl_2^-$	$RSnCl_3Cl^-$
Methyl	240	100 (225)[b]	10	5 (205)	2 (275)
n-Butyl	282	100 (225)	40	12 (247)	3 (317)
Octyl	338	100 (225)	15	18 (303)	2 (273)
Dodecyl	394	100 (225)	45	20 (359)	2 (429)
Phenyl	302	100 (225)	40	96 (267)	3 (337)

[a] RMM, relative molecular mass.

[b] The number in parentheses is the *m/z* value for the ion of the relative abundance cited.



Scheme 1 Fragmentation/reaction scheme for $RSnCl_3$ compounds.

R_2SnCl_2 compounds

For all the compounds studied the $RSnCl_2^-$ anion was the most abundant species detected, whilst ions resulting from the loss of a chlorine atom were absent from the mass spectrum (see Table 4). The chloride anion was readily detectable in all cases, as was the $SnCl_3^-$ anion. This latter species was not derived from impurities or other experimental problems and must therefore originate from an ion–molecule reaction, possibly of the type represented by Eq [4].

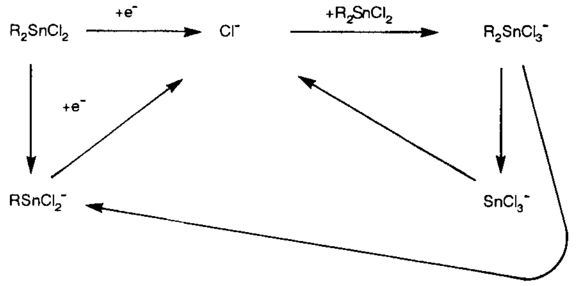
Table 4 Summary of the relative abundance of the major fragment anions from the mass spectra of R_2SnCl_2 compounds

		Relative abundance		
R	RMM	$RSnCl_2^-$	$SnCl_3^-$	Cl^-
Methyl	220	100 (205)[a]	5	20
Ethyl	248	100 (219)	34	28
n-Butyl	304	100 (247)	28	12
Octyl	416	100 (303)	20	5
Dodecyl	528	100 (359)	20	10
Phenyl	344	100 (267)	80	13

[a] *m/z* values are given in parentheses.

$$Cl^- + R_2SnCl_2 \rightarrow R_2 + ClSnCl_2^- \qquad [4]$$

which is somewhat similar to the loss of biphenyl from Ph_2SnCl_2 in the positive-ion mode. A possible series of reactions is shown in Scheme 2. There is no evidence for the biphenyl anion in this work but the large peak at *m/z* 225 ($SnCl_3^-$) in the mass spectrum of diphenyltin dichloride indicates that both the phenyl groups have been replaced by one chlorine atom. In this instance the relative abundance of the $SnCl_3^-$ anion is 80% compared with values of around 20–30% for the other



Scheme 2 Fragmentation/reaction scheme for R_2SnCl_2 compounds.

compounds in the R_2SnCl_2 group. The reactions leading to the formation of $SnCl_3^-$ from a compound containing only two chlorine atoms are currently under investigation in this laboratory using a tandem MS–MS instrument.

Some limited fragmentation of the $RSnCl_2^-$ ions can be seen for both the dioctyl and the didodecyl compounds, where both appear to lose a butene group to give fragments centred on *m/z* 247 and 303 respectively.

R_3SnCl compounds

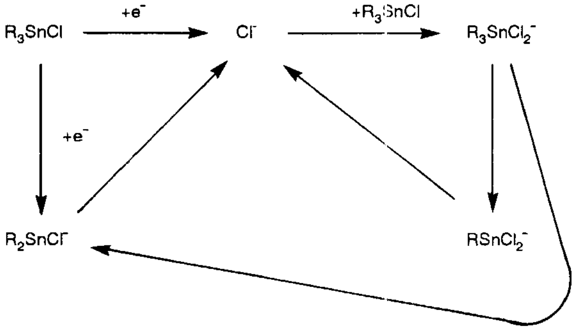
The negative-ion mass spectra of this group of compounds show competition between the R_2SnCl^- and $RSnCl_2^-$ anions for the majority of the charge (see Table 5). For the small alkyl substituted compounds (R = Me, nPr and nBu), the nucleophilic attack of the chloride anion on a neutral molecule followed by the elimination of two alkyl groups (Scheme 3) leads to the most abundant ion but when R is replaced by either the cyclohexyl or phenyl group the chloride anion addition species ($RSnCl_2^-$) is reduced in intensity by a factor of 10. These latter observations are consistent with the fragmentation data cited above (R_2SnCl_2) where the loss of the substituent group gave the most dominant ion for the diphenyl derivative followed by the ion–molecule dialkyl group elimination reaction. Ions resulting from the direct addition of Cl^- to the neutral molecule (negative-ion chemical ionization) are more abundant for this group of compounds with values ranging up to 12% RA. The mass spectrum of the trimethyltin chloride shows a group of peaks at *m/z* 255, ions which can only be derived by the addition of a chlorine molecule to Me_2SnCl^- (m/z 185) to give $Me_2SnCl_3^-$.

Table 5 Summary of the relative abundance of the major fragment anions from the mass spectra of R_3SnCl compounds[a]

		Relative abundance		
R	RMM	R_2SnCl	$RSnCl_2$	$R_3SnCl_2^-$
Methyl	200	35	100	8
		(185)	(205)	(235)
n-Propyl	284	90	100	2
		(241)	(233)	(319)
n-Butyl	326	20	100	5
		(269)	(247)	(361)
Cyclohexyl	404	100	5	
		(321)	(273)	(439)
Phenyl	386	100	15	10
		(309)	(267)	(421)

[a] Molecular ions are less than 20% RA.

[b] *m/z* values based on principal isotopes are shown in parentheses.



Scheme 3 Fragmentation/reaction scheme for R_3SnCl compounds.

Summary of negative-ion mass spectral data

For convenience the eight most intense peaks and the relative abundances recorded in the negative-ion spectra of each of these compounds are detailed in Table 6 in decreasing order of intensity. These results are averaged from many scans recorded as the sample was introduced into the mass spectrometer and represent steady-state ion-source conditions as determined from the ion current monitored at the detector.

DISCUSSION

Negative-ion mass spectrometry led to a smaller range of fragment ions than positive ion MS for all the groups of compounds studied, with one exception. For the R_4Sn compounds there was no detectable negative-ion signal. Comparable frag-

Table 6 Summary of negative ion mass spectral data for selected R_3SnCl, R_2SnCl_2 and $RSnCl_3$ compounds[a]

R_3SnCl									
R = methyl	*m/z*	205	203	207	201	35	185	204	209
	RA[b]	100	70	55	40	32	30	28	25
n-propyl	*m/z*	233	241	231	239	35	235	237	243
	RA	100	90	70	70	65	55	53	35
n-butyl	*m/z*	267	265	269	35	266	271	203	247
	RA	100	70	65	50	32	28	28	25
cyclohexyl	*m/z*	321	319	317	320	323	318	322	325
	RA	100	75	42	38	37	25	20	18
phenyl	*m/z*	309	307	305	311	308	35	304	310
	RA	100	70	38	36	35	25	25	20
R_2SnCl_2									
R = methyl	*m/z*	205	203	207	204	201	209	35	202
	RA	100	68	60	30	28	26	20	15
ethyl	*m/z*	219	217	221	223	215	225	218	35
	RA	100	70	65	43	35	34	32	27
n-butyl	*m/z*	247	245	249	243	225	251	227	223
	RA	100	72	62	32	28	24	17	15
octyl	*m/z*	303	301	305	302	299	307	304	300
	RA	100	78	70	32	31	22	20	15
dodecyl	*m/z*	359	357	361	355	363	356	255	35
	RA	100	70	58	33	25	20	15	12
phenyl	*m/z*	267	225	265	227	269	224	266	229
	RA	100	80	67	58	55	55	33	30
$RSnCl_3$									
R = methyl	*m/z*	225	227	223	229	221	226	222	231
	RA	100	75	74	35	30	18	15	10
n-butyl	*m/z*	225	227	223	35	229	221	226	222
	RA	100	70	70	38	35	30	20	15
octyl	*m/z*	225	227	223	229	221	226	34	231
	RA	100	70	65	36	22	20	15	15
dodecyl	*m/z*	225	227	223	35	229	221	359	226
	RA	100	72	65	45	35	30	20	19
phenyl	*m/z*	225	267	227	265	223	269	35	229
	RA	100	97	72	70	68	57	40	35

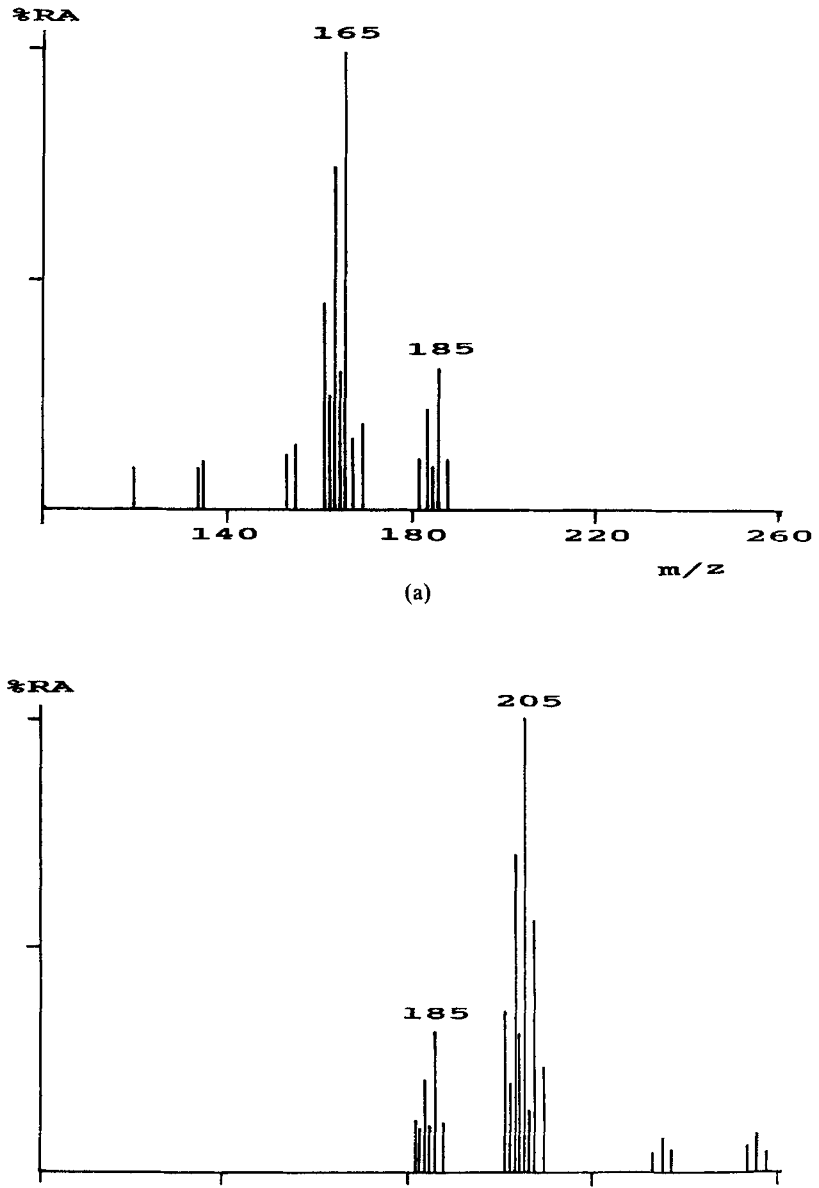
[a] Assignments of peaks may be read from Tables 1, 3, 4 and 5.

[b] RA, relative abundance.

mentation schemes based on electron attachment and/or nucleophilic attack by Cl^- ions were identified for all the chlorine-containing compounds studied. This is an example of an ion–molecule reaction apparently occurring at pressures lower than are conventionally accepted. It is possible that an intermolecular rearrangement was followed by fragmentation to give the observed product.

Comparison of the signal levels monitored for both the positive and negative ions suggests that the detection levels using either method would be similar and not drastically reduced for negative ions as might first be expected, nor much improved as was hoped. Mass spectral data with a sufficient range of *m/z* values to provide unambiguous compound identification were produced for both R_3SnCl and R_2SnCl_2-type compounds but retention-time information would be required for $RSnCl_3$ materials, where the mass spectrometer appeared to be acting in a manner comparable with a tin-specific detector. Typical spectra are compared in Fig. 1(a–d).

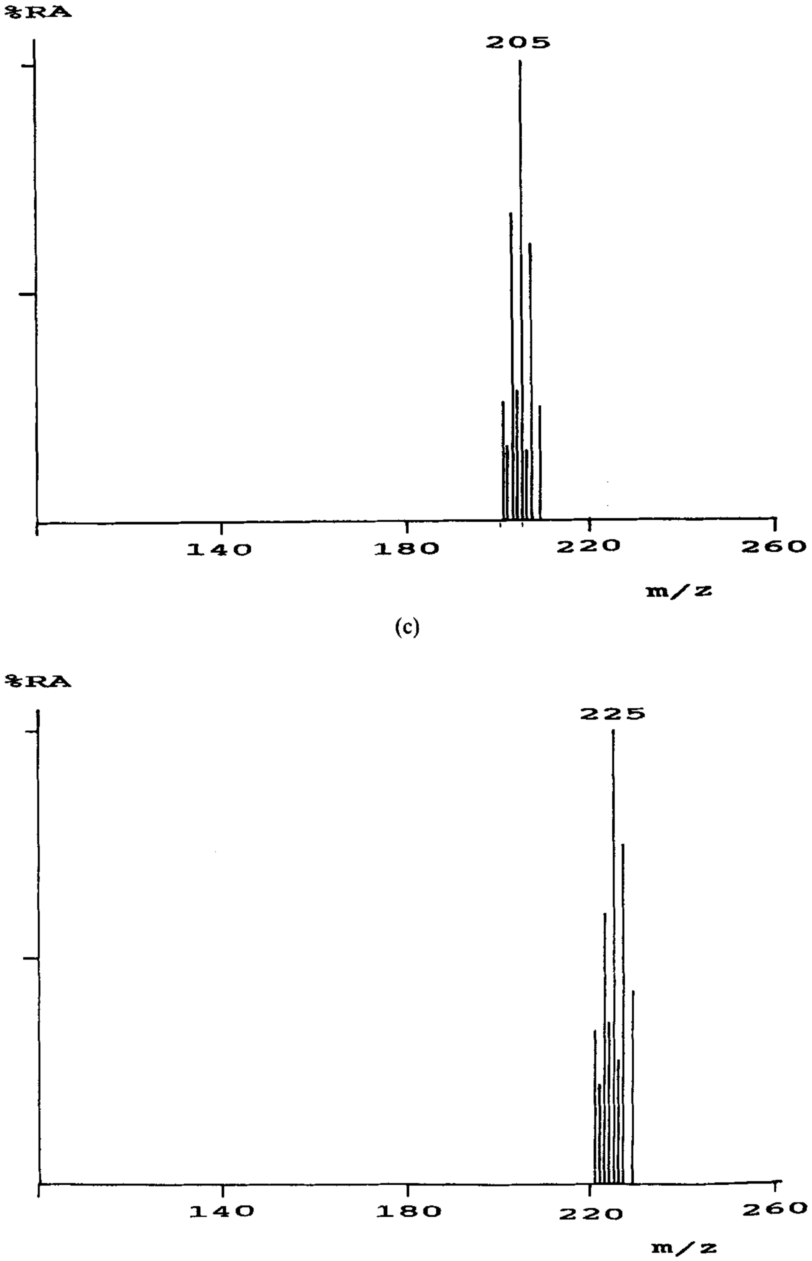
Some of the fragmentation/rearrangement reactions observed suggested that selected tin compounds may have synthetic chemistry applications, particularly in the chemical combination of two substituent groups, such as biphenyl, chlorobenzene etc. The mechanisms leading to these reactions will be probed with MS–MS tech-



(a)

(b)

Figure 1 (a, b) Comparison of the mass spectra for methyltin chloride derivatives (a) Me_3SnCl – positive ions, (b) Me_3SnCl – negative ions.



(c)

(d)

Figure 1 (c, d) Comparison of the mass spectra for methyltin chloride derivatives (c) Me_2SnCl_2- negative ions and (d) $MeSnCl_3-$ negative ions.

niques in order to determine those factors which influence the direction of the fragmentation rearrangement reaction.

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