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Mass spectrometry studies of organolead compounds

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The mass spectra of alkyl-, aryl- and chlorinated -alkyl, aryl organolead compounds were investigated. Positive and negative ion mass spectra of these compounds were recorded using conventional electron impact conditions. In common with the analogous tetraalkyltin and tetraalkylgermanium compounds, tetrabutyllead produced no negative ion spectra under these conditions. The spectra were also examined by tandem mass spectrometry in order to establish reaction mechanisms for these compounds. Fragmentation patterns of seven organolead compounds, based on precursor–product ion relationships, are proposed. Copyright © 2001 John Wiley & Sons, Ltd.

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1 INTRODUCTION

Organolead compounds have wide-ranging toxicological and chemical properties in common with organo-tin and -germanium compounds. Organolead compounds are of great environmental interest. For example, tetraalkyllead (TAL) compounds in air,[1] road dust[2] and rainwater[3] have been trapped and measured using gas chromatography–mass spectrometry (GC–MS) in the single ion monitoring (SIM) mode. Furthermore, there is some evidence for formation of alkyllead compounds in the natural environment from inorganic lead.[4] Various other workers have examined organolead compounds using a variety of analytical methods, including mass spectroscopy.[5,6] However, most of these studies concentrate on identification and measurement of organolead compounds as opposed to elucidating the behaviour of these compounds under electron ionization conditions. A detailed examination of the fragmentation processes for some organolead compounds has been reported.[6] In this case, positive ion electrospray mass spectrometry was performed on trimethyllead and triethyllead species. Fragmentation patterns of these compounds were observed by applying different fragmentation voltages. Much attention has been paid to organotin compounds, many of which are environmental contaminants, and, therefore, mass spectral data for these species are readily available.[7–9] Of the Group IV elements, germanium and tin are similar as they have similar electronic structures (*s, p* and *d* electrons). Consequently, fragmentation processes of organostannanes and organogermanes show several similarities,[10] whereas carbon and silicon (*s* and *p* electrons only) and lead (*s, p, d* and *f* electrons) exhibit different fragmentation routes. Mass spectral investigation of organolead compounds using electron impact (EI) positive and negative techniques in combination with tandem MS (MS–MS) methods was carried out in order to determine: (a) detailed reaction mechanisms for selected organolead compounds in the mass spectrometer; (b) the effect of substitution on fragmentation pathways, particularly replacing an alkyl group with a chlorine atom; (c) the extent of parallel or different reactions between similar lead and tin compounds.

In the MS–MS mode a single precursor ion (fixed *m/z* value) is preselected in the first mass spectrometer and the second mass spectrometer is scanned to determine the collision-induced fragmentation products from that ion. If this investigation commences with the molecular ion of the pure analyte, then the molecular formula of the product

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Table 1 Organolead compounds investigated by EI^+, EI^- and MS–MS techniques

n-Bu_4Pb[a]	Ph_4Pb	Me_4Pb[b]	Et_4Pb[b]
	Ph_3PbCl	Me_3PbCl	Et_3PbCl
		Me_2PbCl_2	Et_2PbCl_2

[a] No EI^- was obtained for this compound.
[b] Literature data EI^+ only. Me_4Pb and Et_4Pb were not investigated as they have been studied by other workers,[11] but their results are included for comparison and completeness.

ion can be determined unambiguously. This allows the fragmentation pathway for each compound to be defined uniquely for these experimental conditions.

2 EXPERIMENTAL

Authentic samples of the organolead compounds, listed in Table 1, were obtained from the Aldrich Chemical Company (>95% purity) and were used without further purification. Samples were introduced into the mass spectrometer *via* the direct insertion probe and, where necessary, the probe was heated in order to vaporize a particular sample. In all cases the probe temperature was less than 100 °C in order to prevent any decomposition of the samples. Mass spectra were first recorded under conventional EI conditions, both in the positive and negative ionization modes, as detailed below.

Having identified the major fragment ions in the EI^+ mass spectrum for each compound, the precursor–product ion (MS–MS) spectra for each of these ions were recorded using a VG Trio 3 triple quadrupole mass spectrometer. The experimental conditions, which have been detailed elsewhere,[8] and the parameters used in the different stages of this investigation are summarized in Table 2.

3 RESULTS

The compounds investigated in this work are detailed in Table 1.

3.1 EI^+ spectra

Examples of the conventional EI mass spectra are shown in Fig. 1 (positive ions) and Fig. 2 (negative ions). As can be seen from Figs 1 and 2, each fragment ion occurs as a group of peaks resulting from the lead isotopes (204, 206, 207 and 208). To simplify the mass spectral fragmentation data, they are presented in terms of the peaks relating to the principal isotope only, namely ^{208}Pb. Similarly, in the case of chlorinated compounds, the data listed are based on ^{208}Pb and ^{35}Cl. The EI^+ mass spectral data for each compound under investigation are recorded in Table 3, which contains details of both the chemical structure of the ion and the relative abundance (RA).

A common feature of the EI^+ mass spectra of these compounds is that very little or no molecular ion is produced; a similar observation was made in the mass spectra of analogous tin compounds.[9] The data in Table 3 indicate some interesting features pertaining to the mass spectra of these compounds,

Table 2 Summary of experimental conditions and parameters

Conventional EI^+ and EI^- conditions	
Mass spectrometer	VG Trio-3, only Q1 operating
Scan rate	*m/z* 35–600 in 1 s
Resolution	>1000
Electron energy	70 eV
Primary ion energy	Instrumental scan mode
MS–MS spectra	
Mass spectrometer	VG Trio-3
Q1	*m/z* values selected from results of standard EI^+ experiments
Q2 collision gas	Argon at 3.5 mT
Q3 scanning *m/z*	20–600 in 1 s
Resolution	>1000
Electron energy	70 eV
Collision energy	8 eV

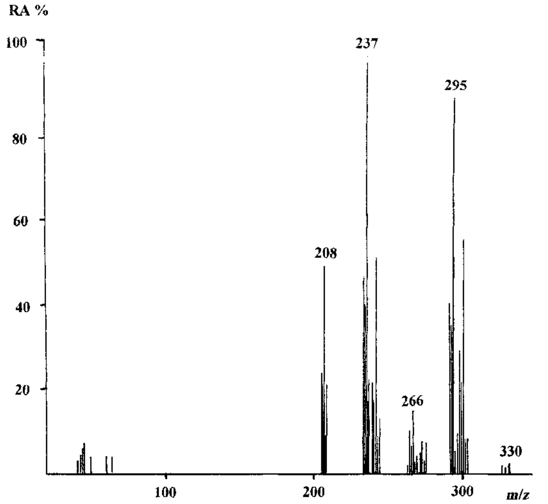

Figure 1 Positive ion mass spectrum of triethyllead chloride.

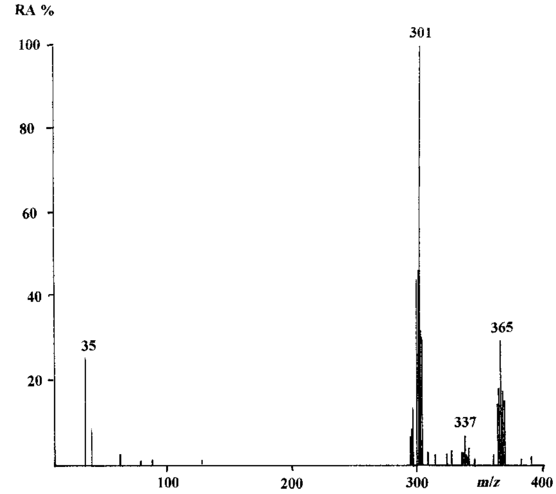

Figure 2 Negative ion mass spectrum of triethyllead chloride.

either as a result of substitution, or when comparison is made with similar tin compounds.

3.1.1 R_4Pb (R = Ph, Me, Et or n-Bu)

Inspection of the data in Table 3 suggests that the major fragmentation for these compounds is the loss of an alkyl/aryl substituent group to produce R_3Pb^+. Further fragmentation reactions seem to be dependent to some extent on the nature of R. The ion corresponding to RPb^+ is more prominent where R = alkyl (RA > 83%), whereas for R = Ph the RA is only 47%. What is also noticeable in the spectrum of *n*-Bu_4Pb is the formation of a relatively small yield of the lead ion (RA = 15%). Tetraalkyl- and tetraphenyl-lead mass spectra produce sizeable ions corresponding to R or its fragmentation products (e.g. for Bu, *m/z* 57,43,41 and for Ph, *m/z* 51,77 are produced). When comparing these spectra with those for the tin analogues,[12] clearly there are some similarities, e.g. the formation of biphenyl ion (*m/z* 154) for both tetraphenyl derivatives. The formation of the mono- and dihydride ions with the associated loss of a neutral alkene molecule(s) was a characteristic of the mass spectra of R_4Sn compounds with alkyl moieties containing two or more carbon atoms.[12] In the mass spectra of tetraalkyllead, the equivalent dihydride ion is nonexistent, whereas the monohydride ion is present at a relatively low RA (10%) for both the ethyl and *n*-butyl compounds.

3.1.2 R_3PbCl (R = Ph, Me, Et)

The EI^+ mass spectra of these compounds show (Table 3) that the major fragmentation process is the loss of the chlorine atom leading to the formation of R_3Pb^+. This is not surprising, since the Pb—Cl bond is the most polar in these compounds. Notwithstanding this common feature, the subsequent fragmentation processes are dependent on the nature of R. For example, when R = Ph, a significant ion (RA = 40%) corresponding to R_2 (biphenyl, *m/z* 154) is formed. In addition, the formation of RPb^+ ion is the preferred fragmentation pathway when R = Et (RA = 100%), whereas this is not so when R = Ph or Me (RA = 20% and 53% respectively).

3.1.3 R_2PbCl_2 (R = Me, Et)

Inspection of the EI^+ mass spectra of these two compounds (Table 3) shows a number of major fragmentation processes. The four most abundant ions are those corresponding to R_2PbCl^+, RPb^+, $PbCl^+$ and Pb^+. The effect of the nature of R is only apparent when considering the order of RA in which these four ions appear in the mass spectra of the dimethyl and diethyl derivatives. The base peaks are at *m/z* 273 (Me_2PbCl^+) when R = Me and *m/z* 237 (EtPb) when R = Et. The introduction of a second chlorine atom seems to have little effect on the major fragmentation pathways of these compounds.

3.2 EI^- spectra

Normally, both positive and negative ions are formed in a conventional EI mass spectrometer.

Table 3 List of EI^+ mass spectral data for compounds used in this investigation based on monoisotopic data from ^{208}pb species and, where applicable, ^{35}Cl

Me_4Pb	RMM 268	*m/z*	253	223	208	239	238			
		RA%	100	85	66	22	2			
		Structure	Me_3Pb^+	$MePb^+$	$Pb^{+\cdot}$	Me_2PbH^+	$Me_2Pb^{+\cdot}$			
Et_4Pb	RMM 324	*m/z*	237	295	208	266	28	27	29	209
		RA%	100	73	61	16	9	7	6	6
		Structure	$EtPb^+$	Et_3Pb^+	$Pb^{+\cdot}$	$Et_2Pb^{+\cdot}$	$C_2H_4^{+\cdot}$	$C_2H_3^{+\cdot}$	$C_2H_5^{+\cdot}$	PbH^+
n-Bu_4Pb	RMM 436	*m/z*	379	265	57	41	43	209	208	323
		RA%	100	83	49	48	47	23	15	10
		Structure	Bu_3Pb^+	$BuPb^+$	$Bu^{+\cdot}$	$C_3H_5^{+\cdot}$	$C_3H_7^{+\cdot}$	PbH^+	$Pb^{+\cdot}$	Bu_2PbH^+
Ph_4Pb	RMM 516	*m/z*	439	208	285	51	77	154	152	362
		RA%	100	49	47	31	14	11	6	3
		Structure	Ph_3Pb^+	$Pb^{+\cdot}$	$PhPb^+$	$C_4H_3^{+\cdot}$	$Ph^{+\cdot}$	Ph_2^+	$C_{12}H_8^+$	$Ph_2Pb^{+\cdot}$
Ph_3PbCl	RMM 474	*m/z*	439	51	154	77	208	285	397	243
		RA%	100	50	40	30	23	20	15	12
		Structure	Ph_3Pb^+	$C_4H_3^{+\cdot}$	Ph_2^+	$Ph^{+\cdot}$	$Pb^{+\cdot}$	$PhPb^+$	Ph_2PbCl^+	$PbCl^+$
Me_3PbCl	RMM 288	*m/z*	253	273	223	243	208	258	238	288
		RA%	100	80	53	51	48	9	8	2
		Structure	Me_3Pb^+	Me_2PbCl^+	$MePb^+$	$PbCl^+$	$Pb^{+\cdot}$	$MePbCl^{+\cdot}$	$Me_2Pb^{+\cdot}$	$Me_3PbCl^{+\cdot}$
Et_3PbCl	RMM 330	*m/z*	237	295	301	243	208	266	272	330
		RA%	100	87	52	48	47	10	7	2
		Structure	$EtPb^+$	Et_3Pb^+	Et_2PbCl^+	$PbCl^+$	$Pb^{+\cdot}$	$Et_2Pb^{+\cdot}$	$EtPbCl^{+\cdot}$	$Et_3PbCl^{+\cdot}$
Me_2PbCl_2	RMM 308	*m/z*	273	208	223	243	258	238	293	209
		RA%	100	91	85	83	15	13	5	4
		Structure	Me_2PbCl^+	$Pb^{+\cdot}$	$MePb^+$	$PbCl^+$	$MePbCl^{+\cdot}$	$Me_2Pb^{+\cdot}$	$MePbCl_2^+$	PbH^+
Et_2PbCl_2	RMM 336	*m/z*	237	243	208	301	209	266	272	
		RA%	100	61	51	47	20	9	5	
		Structure	$EtPb^+$	$PbCl^+$	$Pb^{+\cdot}$	Et_2PbCl^+	PbH^+	$Et_2Pb^{+\cdot}$	$EtPbCl^{+\cdot}$	

Table 4 List of EI$^-$ mass spectral data for compounds used in this investigation based on mono-isotopic data from ^{208}Pb species and, where applicable, ^{35}Cl

Ph_4Pb	RMM 516	*m/z*	439				
		RA%	100				
		Structure	Ph_3Pb^-				
Ph_3PbCl	RMM 474	*m/z*	397	439	35	474	
		RA%	100	95	20	2	
		Structure	Ph_2PbCl^-	Ph_3Pb^-	Cl^-	Ph_3PbCl^-	
Me_3PbCl	RMM 288	*m/z*	323	273	293	35	358
		RA%	100	28	5	3	2
		Structure	$Me_3PbCl_2{}^-$	Me_2PbCl^-	$MePbCl_2{}^-$	Cl^-	$Me_3PbCl_3{}^-$
Et_3PbCl	RMM 330	*m/z*	301	365	35	295	337
		RA%	100	29	27	12	10
		Structure	Et_2PbCl^-	$Et_3PbCl_2{}^-$	Cl^-	Et_3Pb^-	Et_2HPbCl^-
Me_2PbCl_2	RMM 308	*m/z*	273	35	293	243	
		RA%	100	8	3	2	
		Structure	Me_2PbCl^-	Cl^-	$MePbCl_2{}^-$	$PbCl^-$	
Et_2PbCl_2	RMM 336	*m/z*	301	35	336		
		RA%	100	12	2		
		Structure	Et_2PbCl^-	Cl^-	$Et_2PbCl_2{}^-$		

General instrumental designs are such that, usually, only positive ions can be monitored. However, modern instruments are now provided with the ability to monitor ions of both charges. Organolead compounds, in common with similar tin and germanium compounds,[13] show much reduced fragmentation in the negative ion mode. This would suggest that the detection levels would be enhanced for negative ion monitoring, since the total ionization is shared between fewer species. This may be of special interest in molecules where the central atom has available *d* or *f* orbitals, which may stabilize the negative charge.

The EI$^-$ mass spectra, for the compounds under investigation are presented in Table 4, where the *m/z* values for each cluster of peaks are based on the most abundant isotopes of lead and chlorine, namely ^{208}Pb and ^{35}Cl.

Inspection of Table 4 shows one dominant fragmentation process in the EI$^-$ spectra for the compounds under investigation; the exceptions are Bu_4Pb, which yields no EI$^-$ spectrum, and Ph_3PbCl, which gives two major ions. This effect should lead to improved detection capabilities. The high concentration of the base ions and the near absence of other fragment ions is possibly due to stabilization of the negative charge by the *f* orbitals in the lead atom, or that electron attachment is a much lower energy process than the formation of a positive ion.

3.2.1 Ph_3PbR (R = Ph or Cl)

The EI$^-$ spectra of these two compounds indicate the presence of a very stable Ph_3Pb^- ion (*m/z* 439, RA = 100%, when R = Ph and RA = 95% when R = Cl). This is in contrast to the analogous species Ph_3Sn^- and Ph_3Ge^-, which were not detected in the EI$^-$ mass spectra of similar compounds.[10,14] In addition, when R = Cl the base peak is at *m/z* 397 (Ph_2PbCl^-). There is no evidence of ions resulting from either direct or indirect addition of Cl^- to the neutral molecule (negative ion chemical ionization) or any of the fragment ions that are observed for analogous tin compounds.[14]

3.2.2 R_3PbCl (R = Me, Et)

There are differences in the negative ion mass spectra of these compounds. In the case of the trimethyl derivative the spectrum is dominated by an ion (*m/z* 323) formed by the direct addition of a chloride anion to the neutral molecule to yield the ion $Me_3PbCl_2{}^-$.Although a similar ion (*m/z* 365) can be found in the negative mass spectrum of the triethyl derivative (RA = 29%), the most stable ion results from the loss of an ethyl group, giving Et_2PbCl^- (*m/z* 301). The nucleophilic attack of the chloride anion on the neutral molecule followed by the elimination of two alkyl groups is almost nonexistent for this group of compounds, in contrast to analogous tin compounds, where such

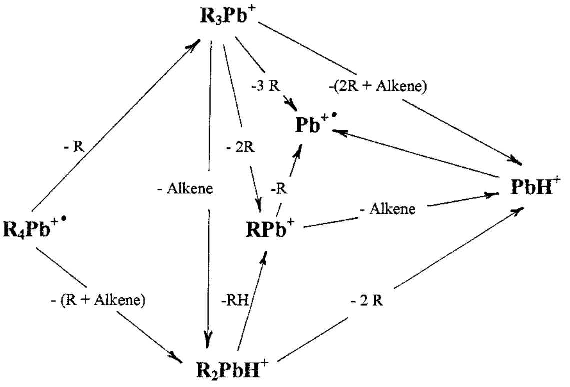

Figure 3 Fragmentation pathway for R_4PB (R = alkyl).

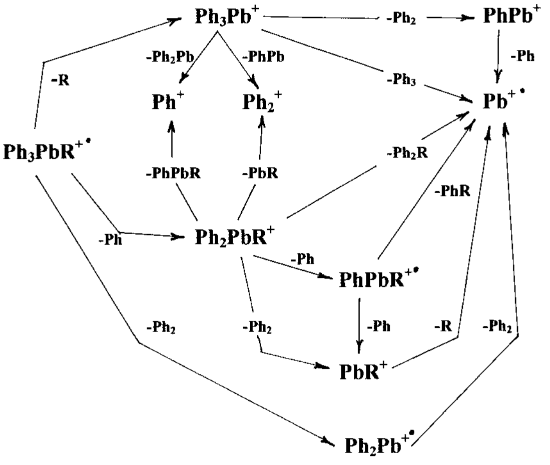

Figure 4 Fragmentation pathway for Ph_3PbR (R = Ph or Cl).

a reaction leads to the formation of the most abundant ion.[14]

3.2.3 R_2PbCl_2 (R = Me, Et)

The $RPbCl_2^-$ anion, i.e. the loss of an alkyl moiety, was the most abundant species detected in the negative mass spectrum of these two compounds, whilst ions resulting from the loss of a chlorine atom were completely absent. In the corresponding tin compounds the $SnCl_3^-$ ion was observed in the negative ion mass spectra,[14] whereas the lead analogue, $PbCl_3^-$, at *m/z* 313 was absent from the mass spectra.

3.3 Positive ion MS–MS studies

MS–MS techniques have been used previously to confirm fragmentation pathways for a range of organtin[9] and organogermanium compounds.[10] A similar approach has now been applied to the organolead compounds under investigation. A precursor ion (fixed *m/z*) was preselected from the EI^+ mass spectra of each compound in the first mass spectrometer, then the second mass spectrometer was scanned in order to determine the fragmentation products from a specific ion. The isotope ^{208}Pb and, where appropriate, ^{35}Cl were used to work out the overall fragmentation patterns. The results were in some cases confirmed by parallel experiments based on the ^{206}Pb isotope. Once the results were collated it was apparent that there was no single reaction pathway common to all the lead compounds in question. Consequently, compounds that gave the same fragmentation pathways in the MS–MS analyses have been grouped together.

3.3.1 Bu_4Pb compound

The MS–MS experiments for this compound indicate that fragmentation occurs *via* the loss of an alkyl or alkene and alkyl group (Fig. 3). The elimination of a butene group from Bu_3Pb^+, leading to the formation of the monohydride species Bu_2PbH^+, does not appear to be the main fragmentation process. The formation of this ion, R_2PbH^+, is seen in both the tetraethyl and tetramethyl compounds, but again at very low RA, typically less than 20%. The preferred fragmentation pathway of the Bu_3Pb^+ ion seems to be the loss of two butyl groups to produce the $BuPb^+$ ion (*m/z* 265). The reaction, whereby the dihydride species is formed as a result of sequential butene loss to form $BuSnH_2^+$, in the mass spectrum of tetrabutyltin is not mirrored in the mass spectrum of the lead analogue. However, the loss of a butene group occurs in other parts of the reaction scheme, e.g. the presence of an ion of *m/z* 209 (PbH^+) is indicative of such a loss from $BuPb^+$.

3.3.2 Ph_3PbR (R = Ph, Cl)

Figure 4 shows a fragmentation pathway based on the MS–MS experiments for these two compounds. The fragmentation pathway does not appear to be affected by substituting a phenyl group with a chlorine atom. The main feature of the fragmentation processes is the loss of a phenyl group or the halogen from the molecular ion to yield Ph_2PbR^+ and Ph_3Pb^+ ions respectively. Both these ions undergo sequential loss of substituent groups to form the various ions shown in Fig. 4. In addition, a biphenyl ion at *m/z* 154 was detected as a reaction

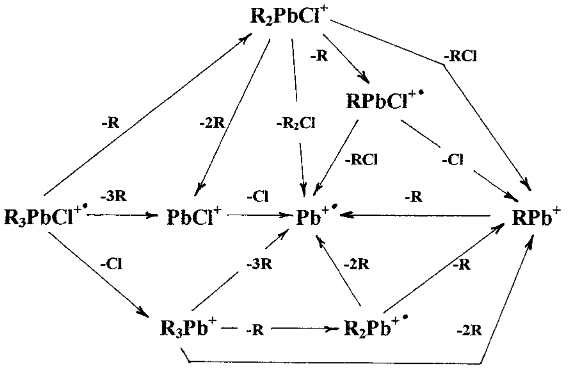

Figure 5 Fragmentation pathway for R_3PbCl (R = Me, Et).

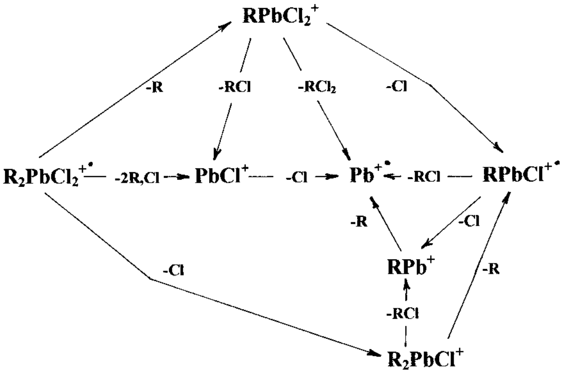

Figure 6 Fragmentation pathway for R_2PbCl_2 (R = Me, Et).

product as a result of apparent rearrangement reactions of Ph_2PbR^+ and Ph_3Pb^+ ions. This is in agreement with similar reaction schemes in the MS–MS studies reported for comparable tin[12] and germanium[10] compounds.

3.3.3 R_3PbCl (R = Me, Et)

The fragmentation pathway for these two compounds in the mass spectrometer based on the MS–MS experiments is shown in Fig. 5. The main feature of this reaction pathway is the initial loss of either one or more R groups or a chlorine atom from the molecular ion followed by sequential loss of the remaining substituents to yield ultimately the $Pb^{+\cdot}$ ion.

3.3.4 R_2PbCl_2 (R = Me, Et)

Figure 6 shows a common fragmentation pathway for these two compounds. It is similar, in many respects, to the reaction pathway for R_3PbCl compounds. For example, there is an initial loss of either an R group or a chlorine atom. In addition, a loss of an R_2Cl group occurs to form the relatively stable ion at *m/z* 243 ($PbCl^+$).

4 DISCUSSION

The EI^+ studies confirm that care is needed when selecting ions of appropriate mass for monitoring TAL species in the environment. The Me_3PbCl and Me_2PbCl_2 compounds and the corresponding ethyl analogues give major peaks in the mass spectra at the same *m/z* values as the tetraalkyl derivatives. This reinforces the data from Nerin and Pons,[1] who reported the occurrence of, for example, *m/z* 223 and 208 for all compounds of the type $R_nR'_{(4-n)}Pb$, where R = Me and R′ = Me or Et. The SIM mode of a GC–MS instrument, set to monitor *m/z* 223 and 208 continuously, rather than scanning over a wider mass range, should, therefore, provide improved detection capabilities for these organolead compounds. The current results demonstrate that the substituted halogen derivatives of these compounds also produce similar mass spectral data, i.e. ions at *m/z* 223 and 208. SIM alone does not, therefore, confirm the presence of an R_4Pb compound, and accurate determination of the appropriate retention times prior to determination of atmospheric TAL levels by GC–MS-SIM in order to identify any contribution from R_3PbCl-type compounds is necessary. The reduced fragmentation in the negative ion mass spectra may lead to increased detection levels, but the absence of any data for Bu_4Pb, and possibly for other tetra- or mixed-alkyl derivatives, renders this approach unsuitable for environmental monitoring.

The MS–MS results show that the fragmentation pathways for compounds are similar within a cognate group, for example R_2PbCl_2 or R_3PbCl. The correspondence of the fragmentation processes between the lead, tin and germanium compounds was shown to be limited, and it was found that many species anticipated from the analogous tin compounds were absent from the lead analogues.

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