Electrospray mass spectrometry of highly moisture-sensitive metal alkoxides

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Electrospray mass spectra of the metal alkoxides $Zr(OEt)_4$, $Ti(OEt)_4$, $Al(OEt)_3$ and $Si(OEt)_4$ and of $Zr(OEt)_4$ after reaction with chelating agents have been recorded in dry ethanol. By adding sodium ethoxide to enhance the formation of ions, well resolved isotope patterns were obtained for each major peak, allowing identification of species. The dominant ions detected in the spectra of $Zr(OEt)_4$ were $[Zr_n(OEt)_{4n+1}]^-$ ($n = 1$–5). Minimal fragmentation was observed at low cone voltages, and the molecular complexity n of the dominant species agreed with the previously established polymeric nature of the alkoxides. Fragmentation of the polymeric Ti and Zr species at high cone voltages occurred by loss of neutral $Ti(OEt)_4$ and $Zr(OEt)_4$. Complexation of $Zr(OEt)_4$ with acetylacetone $[CH_3COCH_2COCH_3]$ (Hacac) yields the monomeric ions $[Zr(OEt)_{4-n}(acac)_n]^-$ ($n = 1$–3) as the dominant species. Hydrolysis and condensation products were observed for 3-sulfanylpropyltrimethoxysilane $[HS(CH_2)_3Si(OC_2H_5)_3]$ reacted with water. The reaction of $Zr(OEt)_4$ with 3-sulfanylpropyltrimethoxysilane resulted in the detection of zirconium alkoxide–silane complexes containing $Zr{-}O{-}Si$ links. ESMS is applicable to the study of transition-metal alkoxide compounds and solution species formed in reactions of these with chelating ligands. The results reveal further opportunities for development of metal alkoxide chemistry.

Metal alkoxides $M(OR)_x$ ($M =$ metal of valency x, $R =$ alkyl or aryl group) are an important class of compounds owing to their success as precursors for the deposition of metal oxides.[1,2] By sol–gel processing or molecular vapour deposition (MOCVD), high purity metal oxides can be prepared for optoelectronics, superconductors and advanced ceramics. Over the past decade organic–inorganic nanocomposites[3] and nanoparticles in glasses and oxides prepared by the sol–gel method[4] have become a rapidly expanding area of research. These new sol–gel materials are designed using precursor mixtures (heterometallic alkoxides)[5] or by chemical modification of the precursors; linking organofunctional groups to the alkoxide with chelating or bridging ligands carrying a functional group, for example carboxylic acids or amino acids.[6] Consequently, there has been a resurgence in the interest of the chemistry of metal alkoxides. The characterisation of metal alkoxides in solution using techniques such as vibrational spectroscopy (IR, Raman) and NMR spectroscopy is often difficult due to the existence of a large range of species which are often oligomeric and have complex structures.

Electrospray mass spectrometry (ESMS) is a relatively new technique which allows ions to be transferred from solution to the gas phase with minimal fragmentation, followed by conventional mass analysis.[7] Initial development of the technique was largely centred around the analysis of large, polar and involatile biomolecules (proteins, peptides)[8] and organic polymers (*e.g.* polyethers).[9–12] However, in recent years the technique has increasingly been used in the study of inorganic and organometallic compounds.[13–16] The ESMS technique is particularly useful for the analysis of systems which are undergoing metal or ligand exchange processes and has frequently been compared with low-temperature NMR spectroscopy.[17–19] The power of the technique in revealing the species present in solution means that reactions of complexes and cluster compounds with a range of species can be conveniently monitored. Studies in inorganic chemistry to date have been concerned with compounds which show appreciable air- and moisture-stability. In principle however, by employing appropriate conditions, ESMS should be equally applicable to the study of highly reactive systems. Recently Michalczyk *et al.* have characterized polyfunctional alkoxysilanes using potassium ionization of desorbed species (K^+ IDS) mass spectrometry.[20] Here we demonstrate that ESMS can be used for the analysis of highly moisture-sensitive main-group and transition-metal alkoxide compounds. The potential to conveniently monitor (by mass spectrometry) solution species formed in the reactions of metal alkoxides with chelating ligands, and metal ion hydrolytic intermediates formed from reaction with water would facilitate the understanding and development of metal alkoxide chemistry.

Experimental

Materials

Zirconium tetrapropoxide [$Zr(OPr)_4$, Aldrich, 70 mass% in propan-l-ol], titanium tetraisopropoxide [$Ti(OPr^i)_4$, Aldrich, 99%], aluminium triisopropoxide [$Al(OPr^i)_3$, Fluka], silicon tetraethoxide [$Si(OEt)_4$, Aldrich, 99%], acetylacetone ($CH_3COCH_2COCH_3$, BDH, 99%), 3-sulfanylpropyltrimethoxysilane [$HS(CH_2)_3Si(OCH_3)_3$, Aldrich, 95%] and 3-aminopropyltriethoxysilane [$H_2N(CH_2)_3Si(OC_2H_5)_3$, Aldrich] were used as received. Samples for ESMS analysis were prepared by dissolving the alkoxide in dry ethanol (the mobile phase solvent) to give a solution typically of approximate concentration 0.1 mmol l^{-1}. The alkoxides, contained in rubber septum-sealed flasks, were transferred to ethanol using a 1 ml syringe. Complete alkoxide exchange to the ethoxide $M(OEt)_x$ occurs as a result of the large excess of ethanol. Hence, this study deals with metal ethoxides only. Sodium ethoxide, prepared by reacting sodium metal with ethanol, was added as an ionisation agent to the samples containing the pure metal alkoxides. The [alkoxide]/[NaOEt] ratio used was typically 40. Dry ethanol mobile phase solvent was obtained by the literature procedure, by refluxing and distillation from magnesium ethoxide, prepared from clean dry magnesium turnings activated with iodine in ethanol.[21] The use of a dry solvent is essential to minimize hydrolysis of the metal alkoxides. Hydrolysis and polycondensation result in the formation of oxo polymers and metal oxides which can potentially cause blocking of the spectrometer capillary systems, but we observed

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no such difficulties during the course of this work. The freshly dried solvent was contained within a parafilm-sealed flask, with no other precautions taken to exclude moisture during the ESMS experiments. 3-Sulfanylpropyltrimethoxysilane was hydrolysed by addition of a slight excess of water to the diluted 3-sulfanylpropyltrimethoxysilane solution in ethanol.

Electrospray mass spectrometry (ESMS)

Electrospray mass spectra were recorded on the freshly prepared sample using a VG Platform II mass spectrometer. The spectrometer employed a quadrupole mass filter with a *m/z* range of 0–3000. The sample solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 µl sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.02 ml min^{-1}. Nitrogen was used as both the nebulising and drying gas, and was produced by liquid-nitrogen boiloff. No other special drying precautions were taken. Skimmer cone voltages were varied from 5 to 180 V. The tendency for ions transferred intact from solution to the gas phase to fragment in the ion source region increases with increasing cone voltage. This allows fragmentation pathways to be studied at high voltage settings. The detection of true solution species requires minimal fragmentation, and this condition was achieved by using a low cone voltage. Confirmation of species was aided by comparison of the observed and predicted isotope distribution patterns. Theoretical isotope distribution patterns were calculated using the Isotope computer program.[22]

Results and Discussion

The metal alkoxides $Zr(OEt)_4$, $Ti(OEt)_4$, $Al(OEt)_3$ and $Si(OEt)_4$

$Zr(OEt)_4$, $Ti(OEt)_4$. The spectra of $Zr(OEt)_4$ in ethanol with no added NaOEt showed peaks due to the ions $[Zr(OEt)_5]^-$ at *m/z* 316 and $[Zr_2(OEt)_9]^-$ at *m/z* 587. However, their intensities were low and several less intense peaks could not be assigned because poor signal-to-noise ratio precluded the recording of isotope patterns for these ions. The $[Zr(OEt)_5]^-$ and $[Zr_2(OEt)_9]^-$ ions originate from the addition of an ethoxide ion OEt^- to the neutral species $Zr(OEt)_4$ and $Zr_2(OEt)_8$, respectively. This suggested that addition of OEt^- to the alkoxide solution would enhance the formation of ions. The signal-to-noise ratio was increased with a factor of *ca.* 50–100 by addition of *ca.* 0.025 mol% sodium ethoxide. High-quality spectra with well resolved isotope patterns for each major peak were subsequently obtained for $Zr(OEt)_4$, $Ti(OEt)_4$ and $Al(OEt)_3$ using this method, with excellent reproducibility of the results. This work extends the application of alkoxide ions as an ionisation reagent in ESMS analyses. The use of this ionisation method has recently been described for the analysis of metal carbonyl complexes which otherwise give poor or non-existent ES spectra.[23]

The negative-ion spectra of $Zr(OEt)_4$, $Ti(OEt)_4$ and $Al(OEt)_3$ and the positive-ion spectrum of $Si(OEt)_4$ are shown in Fig. 1. The species which are detected are listed in Table 1. In all cases complete alkoxide exchange to the ethoxide $M(OEt)_x$ occurs as a result of the large excess of ethanol used

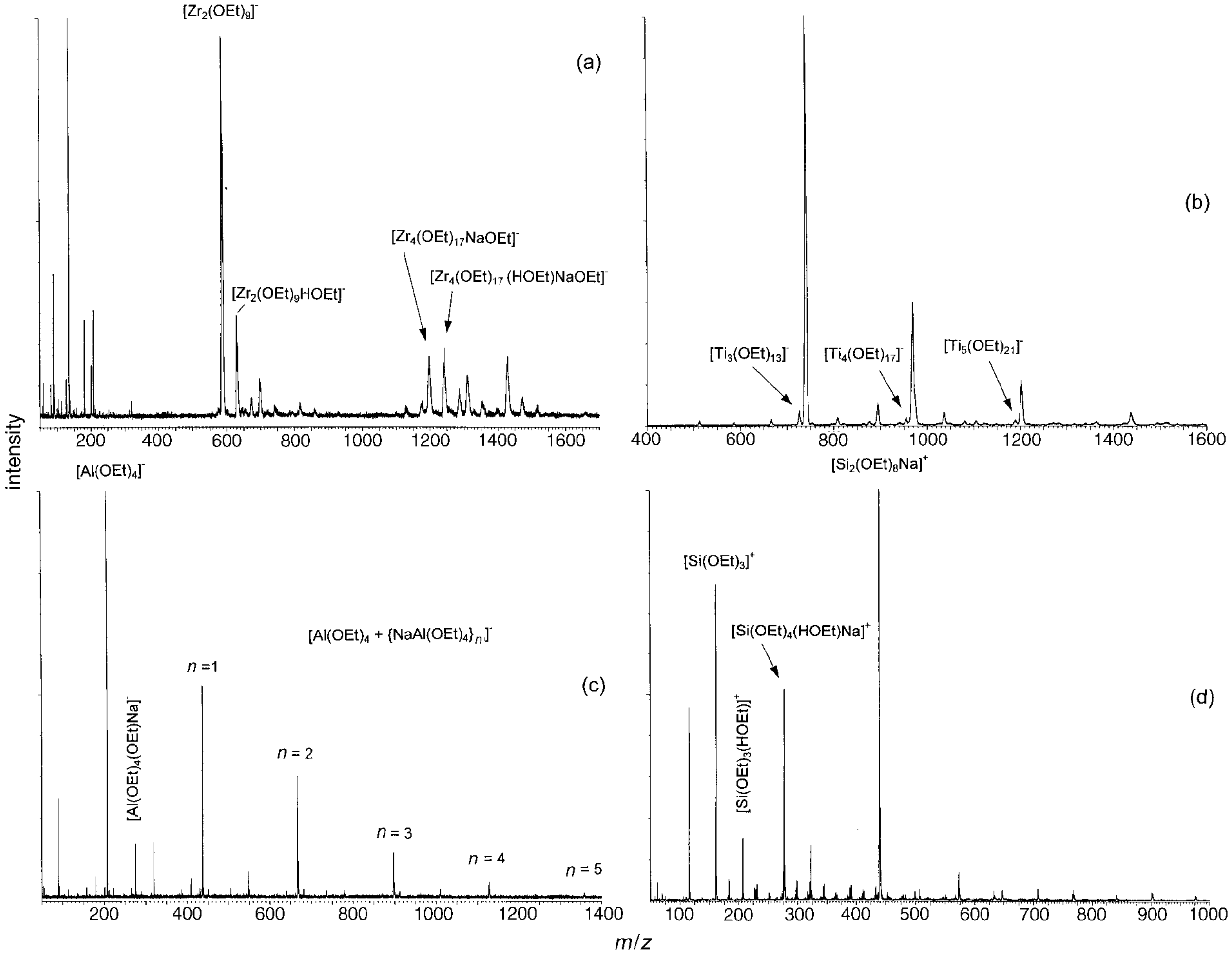

Fig. 1 The negative-ion electrospray mass spectra of (a) $Zr(OEt)_4$ at a cone voltage of 5 V, (b) $Ti(OEt)_4$ at 45 V, (c) $Al(OEt)_3$ at 20 V and (d) the positive ion spectrum of $Si(OEt)_4$ at 5 V. The ethoxides were generated *in situ* by addition of $Zr(OPr)_4$, $Ti(OPr^i)_4$, $Al(OPr^i)_3$ and $Si(OEt)_4$ to dry ethanol.

Table 1 Anionic species detected in the ES mass spectra of $Zr(OEt)_4$, $Ti(OEt)_4$, $Al(OEt)_3$ and $Si(OEt)_4$. Sodium ethoxide was added to the alkoxide solution to enhance the intensity of the spectra (refer to text)

			relative peak height (%)[b]			
compound	ion	*m/z*[a]	5 V	20 V	45 V	90 V
$Zr(OEt)_4$	$Zr(OEt)_5^-$	316	—		35	
	$[Zr_2(OEt)_9]^-$	588	100		100	
	$[Zr_2(OEt)_9HOEt]^-$	634	28		2	
	$[Zr_2(OEt)_9(NaOEt)]^-$	656	—		14	
	$[Zr_2(OEt)_9(HOEt)_2]^-$	680	7		2	
	$[Zr_2(OEt)_9(HOEt)_2NaOEt]^-$	702	11		1	
	$[Zr_4(OEt)_{17}]^-$	1132	2		4	
	$[Zr_4(OEt)_{17}NaOEt]^-$	1199	17		6	
	$[Zr_4(OEt)_{17}(HOEt)NaOEt]^-$	1245	19		3	
	$[Zr_4(OEt)_{17}(HOEt)(NaOEt)_2]^-$	1313	12		12	
	$[Zr_5(OEt)_{21}]^-$	1402	2		4	
	$[Zr_5(OEt)_{21}NaOEt]^-$	1470	5		—	
$Ti(OEt)_4$	$[Ti_2(OEt)_8(OH)_2Na]^{-c}$	512	—	—	1	
	$[Ti_3(OEt)_{13}]^-$	729	—	—	3	
	$[Ti_3(OEt)_{12}(OH)_2Na]^{-c}$	740	—	—	100	
	$[Ti_4(OEt)_{14}(OH)_3Na]^{-c}$	940	6	9	1	
	$[Ti_4(OEt)_{17}]^-$	957	2	9	2	
	$[Ti_4(OEt)_{16}(OH)_2Na]^{-c}$	968	100	100	29	
	$[Ti_5(OEt)_{21}]^-$	1186	—	—	1	
	$[Ti_5(OEt)_{20}(OH)_2Na]^{-c}$	1197	3	10	11	
	$[Ti_6(OEt)_{24}(OH)_2Na]^{-c}$	1425	—	2	1	
	$[Ti_6(OEt)_{23}(OH)_3Na_2]^{-c}$	1436	13	5	3	
$Al(OEt)_3$	$[Al(OEt)_4]^-$	207	100	100	100	100
	$[Al(OEt)_4Na(OEt)]^-$	275	3	13	8	1
	$[Al(OEt)_4+NaAl(OEt)_4]^-$	437	57	52	65	51
	$[Al(OEt)_4+NaAl(OEt)_4NaOEt]^-$	505	2	2	10	—
	$[Al(OEt)_4+(NaAl(OEt)_4)_2]^-$	668	47	29	43	17
	$[Al(OEt)_4+(NaAl(OEt)_4)_2NaOEt]^-$	736	4	1	3	—
	$[Al(OEt)_4+(NaAl(OEt)_4)_3]^-$	898	18	11	10	4
	$[Al(OEt)_4+(NaAl(OEt)_4)_4]^-$	1128	6	4	3	—
	$[Al(OEt)_4+(NaAl(OEt)_4)_5]^-$	1358	1	1	1	—
$Si(OEt)_4$	$[Si(OEt)_3]^+$	163	84			
	$[Si(OEt)_3(HOEt)]^+$	209	14			
	$[Si(OEt)_3(NaOEt)]^+$	232	3			
	$[Si(OEt)_4Na(HOEt)]^+$	277	51			
	$[Si(OEt)_4Na(HOEt)_2]^+$	323	13			
	$[Si_2(OEt)_8Na]^+$	440	100			

[a]The observed *m/z* values are the average of the isotopic mass distribution for the species concerned. [b]Cone voltage indicated. [c]Tentative assignment only (refer to text).

as the mobile phase solvent. Thus, no peaks due to mixed $[M(OEt)_x(OR)_y]^-$ (R = propyl group) ions are observed. The spectrum of $Zr(OEt)_4$ [Fig. 1(a)] is dominated by the $[Zr_2(OEt)_9]^-$ ion at *m/z* 588. Unambiguous identification of this species is provided by comparison of the observed and calculated isotope distribution patterns for the ion, illustrated in Fig. 2. The peak at *m/z* 633 was shown to have an isotope pattern matching that of the $[Zr_2(OEt)_9]^-$ ion. Based on the mass difference of 46 mass units this species can be assigned to $[Zr_2(OEt)_9(EtOH)]^-$, formed from $[Zr_2(OEt)_9]^-$ by the addition of solvent EtOH. The interaction of metal alkoxides with solvent molecules is well known. For example, recrystallisation of $Zr(OPr^i)_4$ from Pr^iOH gives $Zr(OPr^i)_4 \cdot Pr^iOH$.[24] We also note that a peak at *m/z* 89 is observed due to $[HOEt+OEt]^-$. Additional peaks appear at the higher *m/z* values; 1198, 1241, 1311 and 1473. The assignment of these species was aided by the spectrum at 45 V which was stronger and revealed peaks at *m/z* 1130 and 1402 which can be assigned to the tetrameric and pentameric species $[Zr_4(OEt)_{17}]^-$ and $[Zr_5(OEt)_{21}]^-$ respectively. Thus the species observed in the 5 V spectrum can be assigned to $[Zr_4(OEt)_{18}Na]^-$ (*m/z* 1198), $[Zr_4(OEt)_{18}(EtOH)Na]^-$ (*m/z* 1241), $[Zr_4(OEt)_{19}(EtOH)Na_2]^-$ (*m/z* 1311), $[Zr_5(OEt)_{22}Na]^-$ (*m/z* 1473). These ions originate from $[Zr_4(OEt)_{17}]^-$ and $[Zr_5(OEt)_{21}]^-$ by addition of EtOH and/or OEt^- and Na^+. Ion aggregates of this kind are commonly observed in ES mass spectra when a salt is present. The assignments were confirmed by using lithium ethoxide, LiOEt, instead of NaOEt as the ionisation agent. This resulted in shifts of the peaks to lower *m/z* values in agreement with the mass difference between Li and Na.

The 45 V spectrum also showed a dominant peak due to the monomeric $[Zr(OEt)_5]^-$ ion formed from $[Zr_2(OEt)_9]^-$ by loss of one $Zr(OEt)_4$ unit. This ion became increasingly more intense with increased cone voltages up to 90 V. The fact that dissociation occurs by loss of $Zr(OEt)_4$ units is not surprising, as this would result from breaking of the bonds of the bridging ethoxide ligands in the polymeric molecules. At the high voltage of 90 V the spectra contain a range of less intense peaks which were separated by 68 *m/z* units, corresponding to the mass of $[Na^+ + OEt^-]$. Thus, these are due to ion aggregates of metal alkoxide species with one or a multiple of $[Na^+ + OEt^-]$.

The 45 V spectrum of $Ti(OEt)_4$ [Fig. 1(b)] shows four dominant species at *m/z* 740, 968, 1203 and 1436. The observed *m/z* separation of 228 between each of these peaks is consistent with the mass of one $Ti(OEt)_4$ unit. The observed isotope distribution patterns for the peaks agreed with those calculated for the ions $[Ti_3(OEt)_{13}]^-$, $[Ti_4(OEt)_{17}]^-$, $[Ti_5(OEt)_{21}]^-$ and $[Ti_6(OEt)_{25}]^-$. However, the peak positions are slightly higher than the calculated *m/z* values; 729, 958, 1186 and 1414. Only very weak peaks are observed at 729, 958, 1186. The *m/z* values of the dominant peaks are shifted to higher *m/z* values

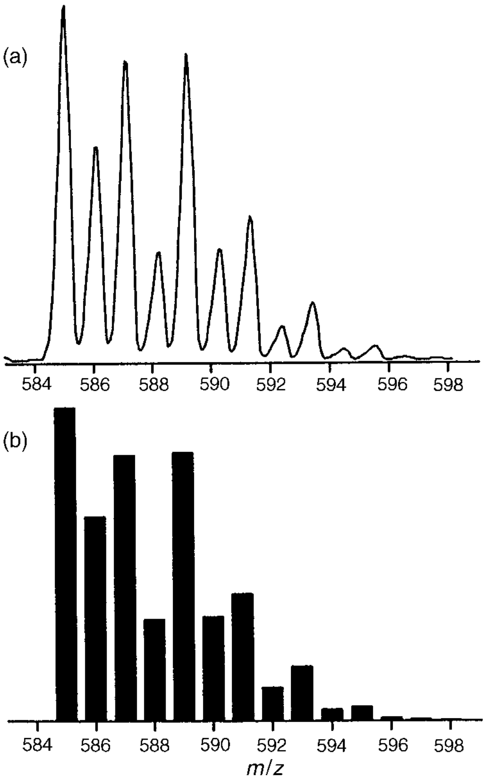

Fig. 2 The isotope distribution pattern for (a) the $[Zr_2(OEt)_9]^-$ peak at *m/z* 588 in Fig. 1(b), and (b) the calculated pattern for the ion

by 11, 12 and 17 units (errors of ±2), respectively. The ions $[Ti_3(OEt)_{12}(OH)_2Na]^-$ (*m/z* 740.4), $[Ti_4(OEt)_{16}(OH)_2Na]^-$ (*m/z* 969.6), $[Ti_5(OEt)_{20}(OH)_2Na]^-$ (*m/z* 1197.7) and $[Ti_6(OEt)_{23}(OH)_4Na_2]^-$ (*m/z* 1437.7) have *m/z* values which fit with the observed peak positions. These ions would result from partial hydrolysis and association with Na^+ ions. However, confirmation of these species was not obtained when lithium ethoxide, LiOEt, was used instead of NaOEt as the ionisation agent. The peaks did not show the expected shifts to lower *m/z* values. The exact nature of these species is therefore not clear. The behaviour of $Ti(OEt)_4$ is in contrast to the clear results obtained for $Zr(OEt)_4$. However, the fragmentation observed at high cone voltages was in accord with that for $Zr(OEt)_4$. The *m/z* 740 peak due to the trimeric ion became more abundant in the 60 V spectrum, consistent with loss of neutral $Ti(OEt)_4$ units from the tetrameric and pentameric ions, whose peaks became less intense. At the high cone voltage of 90 V, an intense peak due to a dimeric monoanion at *m/z* 512 was observed ($[Ti_2(OEt)_8(OH)_2Na]^-$ has *m/z* value 513). It is noteworthy that no peak was observed due to monomeric titanium alkoxide species at this high voltage. By comparison, the $[Zr(OEt)_5]^-$ ion was dominant in the spectrum of $Zr(OEt)_4$ at a cone voltage as low as 20 V. This observation suggests that the polymeric species of $Zr(OEt)_4$ have a greater tendency to fragment compared with those of $Ti(OEt)_4$. This may explain why the dominant ion in the 5 V spectrum was the dimeric species $[Zr_2(OEt)_9]^-$ rather than the trimeric and tetrameric species which would be expected, given that the average degree of polymerization *n* for $[Zr(OEt)_4]_n$ is 3.6.[1] The dominant ions observed in the spectra of $Ti(OEt)_4$ at low cone voltages are the dimeric and trimeric species, consistent with the degree of polymerization of 2.4 reported for $Ti(OEt)_4$.[1] ESMS confirms that these oligomeric alkoxides retain their structural integrity in the gas phase.

$Al(OEt)_3$. The dominant peak observed in the 5 and 20 V negative-ion spectra of $Al(OEt)_3$ is that due to $[Al(OEt)_4]^-$ at *m/z* 207, Fig. 1(c). A series of peaks occur at *m/z* 437, 667, 898 and 1128, each with a separation of 230 *m/z* units corresponding to the mass of $[Al(OEt)_4Na]$. These species can be written as $[Na_n\{Al(OEt)_4\}_{n+1}]^-$ ($n=1$–4). A second much weaker series of peaks occur at positions 68 *m/z* units higher than the $[Na_n\{Al(OEt)_4\}_{n+1}]^-$ ions and can be attributed to aggregation of the $[Na_n\{Al(OEt)_4\}_{n+1}]^-$ ions with $[Na^+ + OEt^-]$. Studies of the molecular complexity of aluminium alkoxides have concluded that aluminium ethoxide is mainly trimeric and tetrameric.[1] At the high cone voltage of 90 V, peaks occur at positions 15, 28 and 45 *m/z* units below the *m/z* 207 peak of $[Al(OEt)_4]^-$, showing loss of CH_3, CH_2CH_3, and OCH_2CH_3 from $Al(OEt)_4^-$ by fragmentation of the ethoxide ion. It is noteworthy that this behaviour was not observed for the alkoxides of Ti and Zr.

$Si(OEt)_4$. An attempt to obtain a negative-ion spectrum of $Si(OEt)_4$ failed. The use of NaOEt did not enhance the formation of negative ions, suggesting that $Si(OEt)_4$ does not readily combine with ethoxide ions to form ions of the type $[M_n(OEt)_{4n+1}]^-$ as was observed for $Ti(OEt)_4$ and $Zr(OEt)_4$. While Ti and Zr prefer to be six- and seven-, and eight-coordinate, Si generally prefers a maximum coordination number of four. This is a likely explanation for the difference in behaviour. However, positive-ion spectra were obtained. The spectrum at a cone voltage of 5 V [Fig. 1(d)] shows a dominant peak due to $[Si_2(OEt)_8Na]^+$ (*m/z* 439). This species most likely originates from neutral $[Si_2(OEt)_8]$ by addition of Na^+. In this case the Na^+ ions aid the generation of charged alkoxide species. The other abundant ions detected are $[Si(OEt)_4(HOEt)Na]^+$ (*m/z* 277), $[Si(OEt)_4(HOEt)_2Na]^+$ (*m/z* 323), $[Si(OEt)_3]^+$ (*m/z* 163), $[Si(OEt)_3(HOEt)]^+$ (*m/z* 207), $[Si(OEt)_3(NaOEt)]^+$ (*m/z* 231).

Alkoxysilanes

Alkoxysilanes, of the type $RSi(OR')_3$ are widely used reagents for the functionalisation of glass and silica surfaces and in the formation of siloxane based polymers.[25] These compounds were expected to be more easily studied by ESMS than $Si(OEt)_4$ owing to the R group which can carry a functional group such as amino or thiol providing charge by accepting or losing a proton.

The positive-ion spectrum of 3-aminopropyltriethoxysilane $[H_2N(CH_2)_3Si(OC_2H_5)_3]$ in dry ethanol solution gave an intense peak due to the $[M+H]^+$ ion $[H_3N(CH_2)_3Si(OC_2H_5)_3]^+$ (*m/z* 221), as might be anticipated as a result of the presence of the basic NH_2 group and a proton source (ethanol). At higher cone voltages (40 V), loss of ethanol occurred yielding the ion $[H_2N(CH_2)_3Si(OC_2H_5)_2]^+$, which is probably an intramolecularly base-stabilised cation. Also observed was a peak due to $[H_3N(CH_2)_3Si(OC_2H_5)_3 + H_2N(CH_2)_3Si(OC_2H_5)_3]^+$ (*m/z* 443). The negative-ion spectrum showed peaks due $[HN(CH_2)_3Si(OC_2H_5)_3]^-$ (*m/z* 220), $[(HOEt)_n + HN(CH_2)_3Si(OC_2H_5)_3]^-$ ($n=1,2$) (*m/z* 265, 310) and the doubly charged ion $[N(CH_2)_3Si(OC_2H_5)_3]^{2-}$ (*m/z* 110). Though not investigated in this study, it is likely that other amino-functionalised silanes would behave similarly.

The negative-ion spectrum of 3-sulfanylpropyltrimethoxysilane $[HS(CH_2)_3Si(OC_2H_5)_3]$ in dry ethanol solution yields an intense peak due to the ion $[S(CH_2)_3Si(OCH_3)_3]^-$ (*m/z* 195). Only very little exchange of the methyl groups of the silane with solvent OEt^- occurred. This is consistent with a high complexation constant for methanol as compared with ethanol and higher alcohols.[1] On addition of water, hydrolysis occurred immediately giving peaks due to the silanols $[S(CH_2)_3Si(OCH_3)_{3-n}(OH)_n]^-$ ($n=1$–3). The diol and triol species ($n=2,3$) were dominant in a freshly prepared mixture containing an excess of water. While the stepwise hydrolysis of alkoxysilanes is fast, the condensation to siloxanes is a much slower process.[25] However within minutes strong peaks due to a range of polymeric condensation species were detected. These include the dimeric $[HS(CH_2)_3Si(OR)_2OSi(OR)_2(CH_2)_3S]^-$ and trimeric $[S(CH_2)_3Si(OR)_2\{OSi(OR)_2(CH_2)_3SH\}_2]^-$ ions with two and three Si—O—Si bridges respectively (R = H, Me, Et). Polymeric species containing up to eight Si atoms were detected. The detection of these siloxanes is facilitated by the presence of the thiol groups which give the species charge by loss of a proton. The ability of functional groups to provide charge is important to consider when attempting to study modified alkoxides and their intermediate hydrolysate and condensation products by ESMS. The association of metal alkoxide complexes with ionisation agents such as the ethoxide ion OEt^- used in this study may not always be sufficiently strong to generate charged species. The fact that we were not able to obtain a negative-ion spectrum of $Si(OEt)_4$ is an example of this. In such cases the use of ligands which contain charged functional groups may aid the formation of ions.

The reaction of $Zr(OEt)_4$ with complexing ligands

Acetylacetone (Hacac). Functional groups that will bind to the metal atoms of metal alkoxides include amino acids, carboxylic acids, β-diketones and β-ketoesters.[1] The β-diketone acetylacetone $[CH_3COCH_2COCH_3]$ chelates through both oxygen atoms and is known to slow down the rate of the hydrolysis and condensation reactions in the sol–gel process.[1] The species observed in the 5 V spectra of reaction mixtures of $Zr(OEt)_4$ and acetylacetone with mole ratios $R = [(Hacac)]/[Zr(OEt)_4]$ of 0.5 and 2.0 are listed in Table 2. For R = 0.5 the ions $[Zr(OEt)_4(acac)]^-$ (*m*/*z* 369) and $[acac]^-$ (*m*/*z* 99) were detected together with the dominant species observed in the spectrum of pure $Zr(OEt)_4$ (see Table 1). Also observed, but much less intense, were peaks due to complexes containing two and three acac ligands; $[Zr(OEt)_3(acac)_2]^-$ (*m*/*z* 425) and $[Zr(OEt)_2(acac)_3]^-$ (*m*/*z* 479), and the dimeric ion $[Zr_2(OEt)_7(acac)_2]^-$ ($m/z = 696$). For $R = 1$ the ions $[Zr(OEt)_4(acac)]^-$ and $[Zr_2(OEt)_8(acac)]^-$ (*m*/*z* 642) became dominant. The $[Zr_2(OEt)_9]^-$ ion was still one of the more abundant species. The spectrum for $R = 2.0$ at a cone voltage of 5 V is shown in Fig. 3(a). This shows only acac-containing species; $[Zr(OEt)_4(acac)]^-$, $[Zr(OEt)_3(acac)_2]^-$, $[Zr(OEt)_2(acac)_3]^-$, $[Zr(OEt)_2(acac)_3Na]^-$, and $[Zr_2(OEt)_7(acac)_2HOEt]^-$, $[Zr_2(OEt)_8(acac)_2Na]^-$, $[Zr_2(OEt)_7(acac)_3Na]^-$. The spectrum is dominated by the monomeric species, which shows that a reduction of the molecular complexity occurs with increasing concentration of acetylacetone. This is consistent with acetylacetone being a poor bridging ligand.

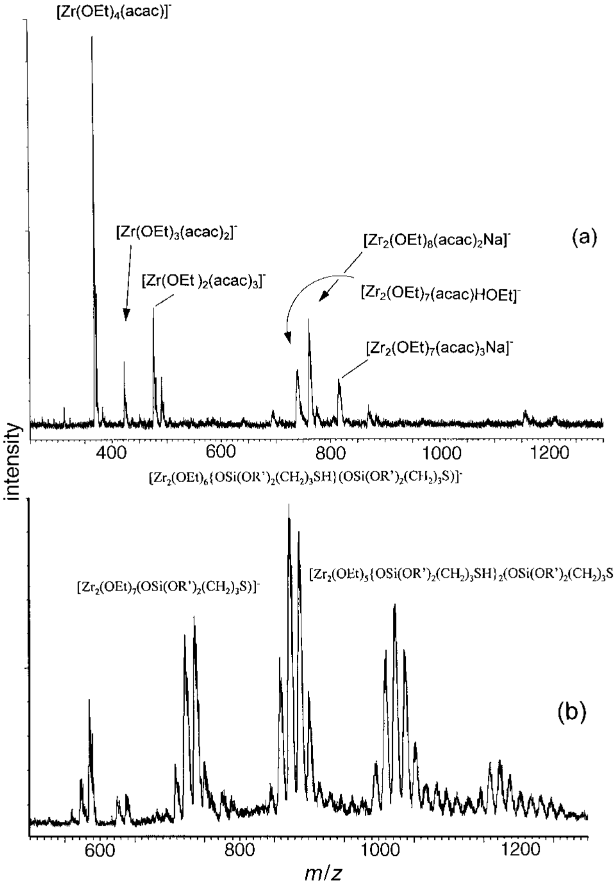

Fig. 3 The negative-ion ES mass spectra (a) of a reaction mixture of $Zr(OEt)_4$ and acetylacetone (Hacac) with mole ratios $R = [Hacac]/[Zr(OEt)_4]$ of 2.0, and (b) of a reaction mixture of $Zr(OEt)_4$ and 3-sulfanylpropyltrimethoxysilane $[HS(CH_2)_3Si(OCH_3)_3]$

In this experiment ethoxide ions, OEt^-, are present in excess in the solvent and act as competing ligands. This may explain the fact that the $[Zr_2(OEt)_9]^-$ ion remained an abundant species for $R = 1.0$. An inert solvent would in most cases be desirable for the analysis of reactions of metal alkoxides with ligands and chelating agents. Acetonitrile, which is a good electrospray solvent, appeared to be unsuitable due to poor

Table 2 Anionic species observed in the ES mass spectra of $Zr(OEt)_4$ reacted with acetylacetone (Hacac) for mole ratios $R = [Hacac]/[Zr(OEt)_4]$ of 0.5 and 2.0. Strong peaks at *m*/*z* 99 and 135 due to $[acac]^-$ and $[(HOEt)_2OEt]^-$ have been omitted to allow a more accurate comparison of the alkoxide species

			relative peak height (%), cone voltage 5 V	
mixture	ion	*m*/*z*	$R = 0.5$	$R = 2.0$
$Zr(OEt)_4 + Hacac$	$[(HOEt)_3OEt]^-$	181	64	40
	$[Zr(OEt)_5]^-$	316	8	5
	$[Zr(OEt)_4(acac)]^-$	370	14	100
	$[Zr(OEt)_3(acac)_2]^-$	425	2	18
	$[Zr(OEt)_2(acac)_3]^-$	479	3	31
	$[Zr(OEt)_3(acac)_2NaOEt]^-$	493	—	15
	$[Zr_2(OEt)_9]^-$	587	100	—
	$[Zr_2(OEt)_9HOEt]^-$	634	23	—
	$[Zr_2(OEt)_7(acac)_2]^-$	696	—	4
	$[Zr_2(OEt)_9(HOEt)_2NaOEt]^-$	702	16	—
	$[Zr_2(OEt)_8(acac)_2]^-$	741	—	14
	$[Zr_2(OEt)_8(acac)_2Na]^-$	764	—	23
	$[Zr_2(OEt)_7(acac)_3Na]^-$	818	—	11
	$[Zr_4(OEt)_{17}NaOEt]^-$	1198	22	—
	$[Zr_4(OEt)_{17}NaOEt(HOEt)]^-$	1241	18	—
	$[Zr_4(OEt)_{17}(NaOEt)_2(HOEt)]^-$	1310	18	—

solubility of the metal alkoxides in this solvent. Tetrahydrofuran (THF) yielded solid precipitates when brought in contact with $Ti(OEt)_4$ and $Zr(OEt)_4$. No ions were observed in either positive- or negative-ion modes, when $Ti(OPr^i)_4$ was analysed in dry hexane solution.

3-Sulfanylpropyltrimethoxysilane [$HS(CH_2)_3Si(OCH_3)_3$]. The species detected with a reaction mixture of 3-sulfanylpropyltrimethoxysilane and $Zr(OEt)_4$ is shown in Fig. 3(b). Four series of peaks occur due to the zirconium alkoxide–silane complexes $[Zr_2(OEt)_{8-n}\{OSi(OR')_2(CH_2)_3SH\}_{n-1}\{OSi(OR')_2(CH_2)_3S\}]^-$ ($R'=Et$, Me; $n=1$–4). The individual peaks within each series which are 14 *m/z* units apart arise from exchange of the silane methoxide groups, OMe^-, with solvent OEt^-. The observed species shows that there is only one Zr—O—Si link with each silane, although in principle all the three oxygen atoms could form bonds. The metal alkoxide remains dimeric as opposed to breaking up into monomeric species which resulted from reaction with acetylacetone. The results show that functionalisation of $Zr(OEt)_4$ with 3-sulfanylpropyltrimethoxysilane readily occur. The synthesis of nanosized gold–silica layered particles has already been achieved using 3-aminopropyltrimethoxysilane $NH_2(CH_2)_3Si(OCH_3)_3$ as a coupler.[26] The amino groups bind to the gold surface by gold–amine bonds and the silanol groups $Si(OH)_3$, formed by hydrolysis of the $Si(OCH_3)$ groups, react with silicate SiO_3^{2-} with the release of water generating a silica layer, SiO_2. By analogy with this method, the formation of a TiO_2 or ZrO_2 oxide layer should be possible by binding the alkoxides $Ti(OEt)_4$ and $Zr(OEt)_4$ instead of SiO_3^{2-}, followed by hydrolysis. Thiolate ligands, RS^-, are useful capping ligands for nanoclusters of group II–VI semiconductor materials. The coating of such particles with an oxide layer of TiO_2 or ZrO_2 may therefore be possible using thiolsilanes such as 3-sulfanylpropyltrimethoxysilane. Combining a small bandgap semiconductor with a large bandgap semiconductor offers opportunities to sensitize the latter, which may find applications in photocatalysis, solar energy conversion, *etc.*

Conclusions

We have demonstrated that electrospray mass spectrometry is a viable technique for the investigation of moisture-sensitive metal alkoxide compounds. The neutral metal alkoxide compounds give poor spectra, but this can be overcome by using ionisation agents such as alkoxide ions, cations and ionic ligands which form charged adducts. The technique has considerable potential for monitoring solution species formed in the reactions of metal alkoxides with chelating ligands and detecting intermediate hydrolysis products.

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