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Application of electrospray ionisation mass spectrometry to the study of dilute aqueous oligomeric anions and their reactions

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For the first time, electrospray ionisation mass spectrometry has been carried out on purely aqueous solutions of anions, specifically dilute (10^{-3} mol dm^{-3}) isopolytungstates, peroxotungstates and heteropolymolybdates and tungstates. Many new species have been detected that have not previously been reported in water, including $[W_6O_{19}]^{2-}$ and $[W_2O_7]^{2-}$. To demonstrate its investigative potential, the method was used to identify the complex and previously uncharacterised reaction products from the reaction of H_2O_2 on powdered tungsten metal, where hexametalates form with up to four peroxo ligands, and also to track kinetic processes such as the course of metal-ion exchange between phosphododecametalates, and the attack of H_2O_2 on paratungstate B.

Aqueous polyoxometalate anions and their corresponding acids are important in many areas of chemistry and biochemistry. For example, heteropolyanions such as tungsto- and molybdophosphates and -silicates have a wide application in catalysis,[1a–f] and even as antiviral agents to treat HIV.[2] Other applications of Group 5 and 6 metal oxide complexes may be found in solar energy conversion[3–6] and the breakdown of lignin in paper production.[7,8]

However, they are difficult to characterise, particularly in aqueous solutions, where most of them are initially formed as equilibrating mixtures. Thus they provide a challenging test-bed for any new technique able to detect inorganic anions under chemically realistic conditions. Many studies have relied on X-ray crystallography or on NMR spectroscopy. Only a few polyoxoanions crystallise without disorder, however, and the available NMR nuclei in such complexes are mostly of low sensitivity. Raman spectroscopy, optical spectrophotometry and polarography are of use for relatively simple mixtures, but have limited ability to discriminate between different anions. Raman spectra also require fairly high concentrations. Potentiometry does have the ability to investigate moderately dilute solutions, but it depends upon the attainment of equilibrium, often problematic with *e.g.* polytungstates, and it cannot be applied to kinetic studies or to unstable products such as peroxometalates. Thus there is great need for new and preferably rapid methods for the study of complex, aqueous solutions of polyoxoanions, or of their reactions, particularly in small quantities and in the very dilute solutions that are relevant to *e.g.* biological or environmental studies. Here we investigate the potential of electrospray ionisation mass spectrometry (ESIMS) to provide such a method.

Mass spectrometry has already been found to be a useful tool for the analysis of polyoxoanions, where these have been trapped in a solid matrix. Finke *et al.*[9,10] examined positive and negative heteropolytungstate complexes, by means of fast atom bombardment (FAB) mass spectrometry. In a further study of polyoxoanions using this technique, Trovarelli and Finke[11] showed that in the positive-ion spectra few fragment peaks were observed, whereas the negative-ion spectra showed abundant fragment peaks.

More recently, it has been shown that ESIMS may be used in the analysis of polyoxometalates dissolved in organic or aqueous–organic solvents.[12–14] It has the considerable advantage of being a very gentle process for producing ions. A solution of the anions (or cations) in question, usually 1 mmol dm^{-3} or less, is formed into an extremely fine spray of droplets, whose fineness and hence evaporation rate is greatly enhanced by appropriate electrostatic charging at the outlet needle. A further modest accelerating voltage, typically 35 V, is necessary within the ion source, to separate the ions with the desired sign of charge from the rest, and to break away any weakly attached solvent clusters. This ‘cone’ voltage does not lead to significant chemical effects, although the evaporation process does inevitably involve rapidly changing concentrations and pH.

Le Quan Tuoi and Muller[13] first observed singly, doubly and triply charged heteropolytungstate and molybdate anion peaks in ESI spectra and found that the isotopic distributions of the complexes were very similar to the calculated distributions. Lau *et al.*[14] studied a similar set of complexes by means of ESIMS and performed collision-induced dissociation experiments on the intact ions, in order to obtain structural information. All these studies involved organic solvents. However, water is a very desirable solvent for the general analysis of aqueous polyoxoanions because it allows comparisons with the results of potentiometric measurements, and reduces the formation of strong ion pairs and of *e.g.* alkoxo complexes. In addition, organic solvents are vulnerable to oxidation, especially when peroxides are added. We have therefore developed methods for working with purely aqueous solutions.

In aqueous solutions above pH 8, tungsten- and molybdenum-(VI), M, exist as the monomeric anions $[MO_4]^{2-}$. Upon the addition of acid and *e.g.* phosphate, these undergo condensation reactions to yield dodecametalate heteropolyanions, by reactions such as (1). Many of the heteropolyanions examined

$$23H^+ + [HPO_4]^{2-} + 12[MO_4]^{2-} \longrightarrow [PM_{12}O_{40}]^{3-} + 12H_2O \quad (1)$$

in this study, typically $[H_xPM_{12}O_{40}]^{(3-x)-}$, have the α-Keggin structure, which consists of four sets of three octahedral units of the type MO_6, fused at some edges and vertices to form an approximate sphere around the central phosphate unit. Intermediate lacunary Keggin species of nominal formula $[H_3PM_{11}O_{39}]^{4-}$ are also well known and are believed to be intermediates in the stepwise process of metal exchange between PM_{12} polyoxoanions.[15] These anions lack one of the above 12 octahedra and their precise state of protonation is not certain. They are disfavoured at low pH, presumably because of their higher charge. In the absence of phosphate, tungstate isopolyanions form. These may also possess Keggin structures, with one or two H^+ ions in the central cavity previously occupied by P^V, but at pH 5–7 the dominant isopolytungstates, namely the W_7 anion paratungstate A and the W_{12} anion paratungstate B, have two somewhat less symmetrical structures.[15,16] At lower pH one might also hope to detect the tungstate Y anion $[H_2W_{10}O_{32}]^{2-}$. The presence of other anions, such as the dimer $[W_2O_7]^{2-}$ and the hexamer $[W_6O_{19}]^{2-}$ might also be suspected in slightly acid solutions, by extrapolation from studies in non-aqueous solutions, but such species have not been reported to date, possibly because they are of low solubility.[15]

We report below that all these aqueous species, and others, are indeed detectable by ESIMS. Thus we can confirm that ESIMS is a viable technique for the identification of very dilute aqueous polyoxometalate anions. We also evaluate its interpretability and show that it may be used to follow reaction processes which occur in solution, on a time-scale of minutes.

Experimental

Mass spectrometry

All experiments were performed in a Quattro II Q*h*Q tandem quadrupole instrument (Micromass, Manchester, UK) fitted with an electrospray ionisation source operated in negative-ion mode. The tip of the capillary and the sampling cone were maintained at potentials of −3 kV and −35 V respectively, relative to ground. The source temperature was 80 °C. The mobile phase consisted of water with no additives. Its optimum flow rate was found to be 10 μl min^{-1}. A Rheodyne injector fitted with a 20 μl loop was used to inject the sample solution into the flow of the mobile phase.

Mass spectra were acquired by scanning the first quadrupole mass analyser from *m*/*z* 2000 to 100 and ions were detected by means of a scintillator detector positioned after the first quadrupole analyser. Approximately 25 scans were summed to give mass spectra. All data were processed by means of the Micromass Masslynx data system.

Sample preparation

Aqueous solutions were prepared from standard laboratory chemicals (BDH and Aldrich) generally as sodium salts. Lithium salts, however, were prepared by the action of $LiOH\cdot H_2O$ on WO_3, for the preparation of paratungstate B, and equimolar LiCl was added to maximise its formation relative to paratungstate A. The mixed-metal solutions were prepared simply by mixing the aqueous tungsten and molybdenum phosphododecametalate solutions (10^{-3} mol dm^{-3}). Some further, minor dilution may occur as the injected bolus spreads as it is driven from the injection loop towards the heated, stainless-steel capillary. The nature of the ESI process makes it impossible to be sure of the exact concentration or pH at the moment the anion becomes isolated from other anions, for ESI is inherently a process of electrolysis, evaporation and charge-sorting, and the sizes and charges of the evaporating droplets are still the subject of controversy. Hence the pH values and concentrations, quoted below, apply only to the solutions before injection. Despite these limitations, the data below show that the spectra correlate well with the known chemistry of the solutions studied, once allowance is made for the unavoidable effects of the final desolvation.

The reaction of metallic tungsten powder with H_2O_2 was carried out using the procedure of Kudo *et al.*[17] The procedure for the kinetic study of the mixed-metal species is discussed in a subsequent section.

Results and Discussion

Single anions

Fig. 1(*a*) is a partial mass spectrum of a 1 mmol dm^{-3} aqueous alkaline solution (pH *ca.* 9) of sodium tungstate. The only species known to be present initially is the $[WO_4]^{2-}$ anion. However, the spectrum in fact predominantly shows the protonated tungstate anion, $[HWO_4]^-$, together with minor amounts of $[NaWO_4]^-$, for reasons discussed below. Both anions contain four main tungsten isotopes (^{182}W, 26.3; ^{183}W, 14.3; ^{184}W, 30.67; and ^{186}W, 28.6%) and the corresponding isotope distribution is evident. It provides a useful fingerprint and allows the rapid identification of tungsten-containing ions in the mass spectra. The isotope patterns of polyoxometalate anions which contain more than one tungsten atom are more complicated because of the additional number of combinations of isotopes which the species contain. For example, Fig. 1(*b*) shows the mass spectrum from a pH 2.7, aqueous solution of sodium phosphododecatungstate, 1.0 mmol dm^{-3} in W. The spectrum largely arises from the $[PW_{12}O_{40}]^{3-}$ species and also the doubly charged protonated species, $[HPW_{12}O_{40}]^{2-}$. Each of these anions contains twelve tungsten atoms and, consequently, the number of combinations of isotopes present in these anions is large. A quadrupole analyser is not capable of resolving each doubly charged monoisotopic ion and, therefore, the molecular ion peaks shown in Fig. 1(*b*) are broad.

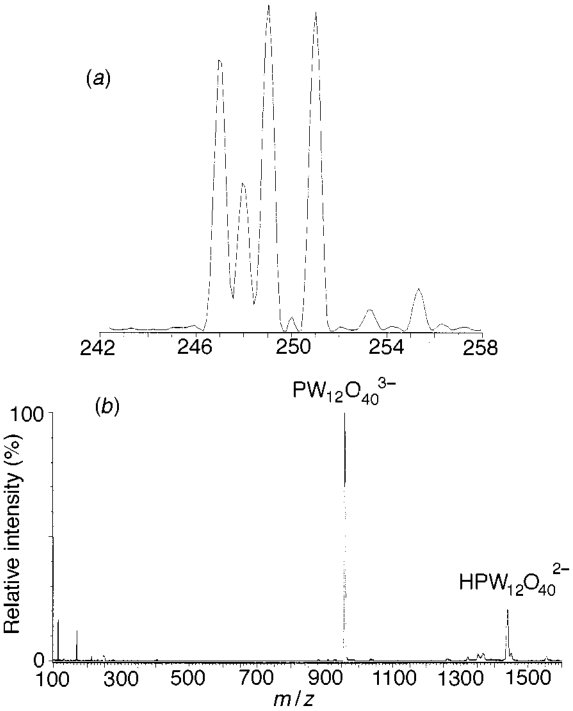

Fig. 1 The ESI mass spectra of (*a*) the protonated tungstate anion, $[HWO_4]^-$, showing the distinctive isotope pattern of tungsten and (*b*) phosphododecatungstate showing the doubly and triply charged species. Both aqueous solutions were 1 mmol dm^{-3} in W. The initial pH values were *ca.* 9 and 2.7 respectively

Molybdenum-containing anions display a similarly distinctive isotope pattern (^{92}Mo, 14.84; ^{94}Mo, 9.25; ^{95}Mo, 15.92; ^{96}Mo, 16.68; ^{97}Mo, 9.55; ^{98}Mo, 24.13; and ^{100}Mo, 9.68%) in ESI mass spectra, as shown by the partial mass spectrum of the molybdate anion in Fig. 2(*a*), also obtained from an alkaline, 1 mmol dm^{-3} solution. Again, the mass spectra of the larger polyoxometalate species, acquired from a solution 1.0 mmol dm^{-3} in Mo, at pH 2.9, show two main broad peaks which are attributed to the $[PMo_{12}O_{40}]^{3-}$ and $[HPMo_{12}O_{40}]^{2-}$ species [Fig. 2(*b*)].

Mixed-metal species

To our knowledge, mixed-metal polyoxoanion species of the type $[H_xPW_nMo_{12-n}O_{40}]^{(3-x)-}$ have not previously been characterised by mass spectrometry techniques in any solvent. Previous ^{17}O and ^{183}W NMR studies have characterised many aqueous mixed-metal isopolymetalate species, *i.e.* with no central P. These generally span all possible metal combinations, provided that the two single-metal species are isomorphous. For example, at pH *ca.* 6 tungstate solutions are an equilibrium mixture

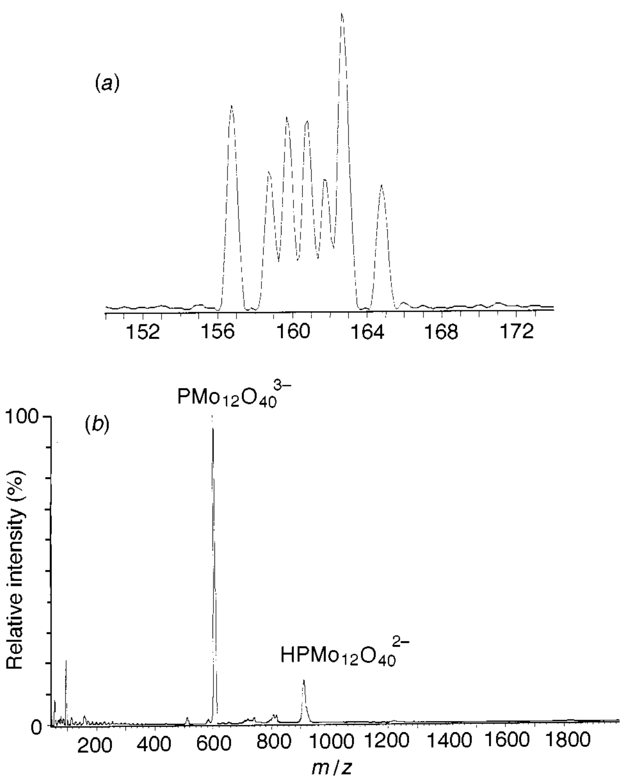

Fig. 2 The ESI mass spectra of (*a*) the protonated molybdate anion, $[HMoO_4]^-$, and (*b*) phosphododecamolybdate. Both aqueous solutions were 1.0 mmol dm^{-3} in Mo. The initial pH values were *ca.* 9 and 2.9 respectively

of paratungstate A, $[W_7O_{24}]^{6-}$, and paratungstate B, $[H_2W_{12}O_{42}]^{10-}$, although molybdate at a similar pH forms only the first, heptametalate structure. Hence if molybdate is added to tungstate at pH 6 one finds the complete range of heptametalates $[Mo_nW_{7-n}O_{24}]^{6-}$ where $n = 0$–7, whereas only the monosubstituted dodecametalate species $[H_2MoW_{11}O_{42}]^{10-}$ is detected.[18,19] One would therefore expect to obtain a complete range of mixed-metal species upon equilibration of phosphododecamolybdate with phosphododecatungstate.

Fig. 3 is an ESI spectrum of a fully reacted, aqueous mixture of phosphododecamolybdate and phosphododecatungstate (pH 2.8) with tungsten 4.0 mmol dm^{-3} and molybdenum 2.0 mmol dm^{-3}. This shows an entire range of mixed-metal phosphate-centred α-Keggin anions. There are two main distributions of peaks, from doubly and triply charged species. Each peak within a distribution corresponds to one of the various proportions (of which there are thirteen) of molybdenum and tungsten atoms which form the cluster ion. The *m*/*z* values of the possible ions are displayed in Table 1. The doubly charged ions may be written as $[HPW_nMo_{12-n}O_{40}]^{2-}$, while the loss of a proton from the complex gives rise to the triply charged species.

A third and fourth series of peaks is also observed at lower intensity in Fig. 3. These series arise from lacunary anions, with masses corresponding to the general gas-phase formulae $[HPM_{11}O_{37}]^{2-}$ and $[PM_{11}O_{37}]^{3-}$. Such lacunary species are known to form in solution, *i.e.* independently of the ESI process, although these aqueous species may well be more highly hydrated. The formation of lacunae is favoured under less acid conditions and in dilute solutions, and is thought to provide a mechanism for metal exchange in solution.[15]

Table 1 Values of *m*/*z* possible for mixed-metal phosphododecametalates and lacunary phosphoundecametalates

W atoms in anion	Mo atoms in anion	Mean *m*/*z*	
		with *z* = 3	with *z* = 2
Dodecametalates[a]			
12	0	959.1	1439.1
11	1	929.7	1395.1
10	2	900.4	1351.1
9	3	871.1	1307.2
8	4	841.8	1263.2
7	5	812.5	1219.3
6	6	783.2	1175.3
5	7	753.9	1131.4
4	8	724.6	1087.4
3	9	695.3	1043.5
2	10	666.3	999.5
1	11	636.7	955.5
0	12	607.4	911.6
Lacunary undecametalates[b]			
11	0	881.4	1322.6
10	1	852.0	1278.6
9	2	822.7	1234.6
8	3	793.4	1190.7
7	4	764.1	1146.7
6	5	734.8	1102.8
5	6	705.5	1058.8
4	7	676.2	1014.9
3	8	646.9	970.9
2	9	617.6	927.0
1	10	588.6	883.0
0	11	559.0	839.0

[a] General formulae $[HPW_nMo_{12-n}O_{40}]^{2-}$ and $[PW_nMo_{12-n}O_{40}]^{3-}$, with $n = 0$ to 12. [b] General formulae $[HPW_nMo_{11-n}O_{37}]^{2-}$ and $[PW_nMo_{11-n}O_{37}]^{3-}$, with $n = 0$ to 11.

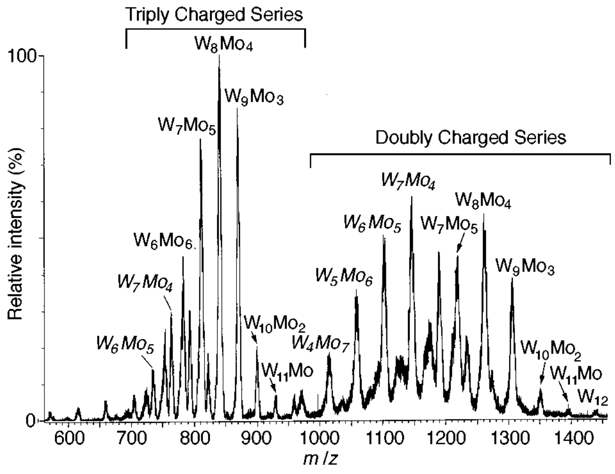

Fig. 3 The ESI mass spectrum of a fully reacted mixture of phosphododecatungstate and phosphododecamolybdate, initially 6.0 mmol dm^{-3} in W + Mo, pH 2.8. Species are identified in abbreviated form, corresponding to the numbers of metal atoms in the fuller, text formulae. Lacunary anions are italicised, for visual convenience

Kinetics of exchange

The spectrum in Fig. 3 only shows the end result of the equilibration process in which the two polyoxometalate species $[H_xPW_{12}O_{40}]^{(3-x)-}$ and $[H_xPMo_{12}O_{40}]^{(3-x)-}$ interchange metal atoms to form anions which have different *m*/*z* ratios. No indication of the rate of this equilibration can be obtained from examination of this spectrum alone. Also, it was necessary to confirm that the metal exchange process occurred in the initial mixture, and not simply as an artefact of the ESIMS process. Hence, a study of the time dependence of the proportions of the ions containing the two metals was carried out. This involved mixing aqueous solutions of the two separate tungsten and molybdenum complexes, each 2.0 mmol dm^{-3} in metal, and acquiring spectra of the reaction mixture over a period of 45 min. The mixture was acidified in this case to pH 1.8, in order to minimise the exchange rate. The mass spectrum in Fig. 4(*a*) was acquired 2 min after the two solutions were mixed (the time

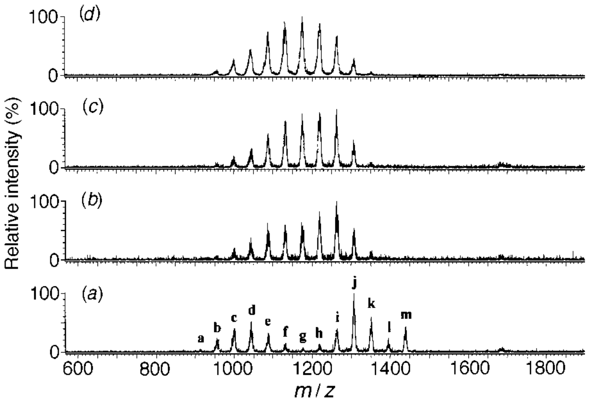

Fig. 4 The ESI mass spectra of mixtures of phosphododecatungstate and phosphododecamolybdate acquired (*a*) 2, (*b*) 17, (*c*) 32 and (*d*) 47 min after the two solutions were initially mixed. Initially 1 mmol dm^{-3} in each metal, pH 1.8. Labels **a**–**m** correspond, in order, to the formulae $[HPW_nMo_{12-n}O_{40}]^{2-}$ with $n = 0$ to 12

taken for the sample to flow from the injector to the tip of the capillary) and shows two distinct distributions of mixed-metal anions. It is noticeable that the two complexes have interchanged metal atoms with one another and that the most intense peak after 2 min is due to the $[HPW_9Mo_3O_{40}]^{2-}$ ion. The acidification has also suppressed the lacunary species and also the formation of trinegative ions in the gas phase. If it were possible to acquire a mass spectrum at the instant the two metal species are mixed, it is predicted that two single composite peaks would be observed [similar to Fig. 1(*a*) and 1(*b*)], due to the individual $[HPMo_{12}O_{40}]^{2-}$ and $[HPW_{12}O_{40}]^{2-}$ anions. Further spectra were acquired at 15 min intervals over a period of 45 min [Fig. 4(*b*)–4(*d*)] during which time the distribution of the metal species within the anions reaches equilibrium. After 45 min the most intense peak in the spectrum corresponds to the doubly charged ions which have an equal number of tungsten and molybdenum atoms, that is $[HPW_6Mo_6O_{40}]^{2-}$.

The kinetic process may in fact be approximately modelled for all peaks, except for PW_{12}, by assuming constant probabilities for any of the $PM_{11} \longleftrightarrow PM_{12}$ metal transfers. However the PW_{12} anion dissociates noticeably more slowly than the others, as can be seen from examination of the intensity of this ion's peak in Fig. 4(*a*). This observation is expected because, in general, tungstates are less labile than molybdates. The above experiments show that it is possible to track equilibration processes of polyoxometalate mixtures with time, providing that the equilibration occurs over a reasonably long (minutes) timescale.

Isopolytungstates with high mass

The ESIMS technique was also attempted on aqueous paratungstate, using a solution 10 mmol dm^{-3} in W, at pH 6.2. The dominant species in the stock solution, 2.0 mol dm^{-3} in W and in LiCl, had earlier been shown by ^{183}W NMR spectroscopy to be very largely paratungstate B.[16] This has the nominal formula $[H_2W_{12}O_{42}]^{10-}$, which is an improbably high charge to exist in the gas phase, for an anion of this size, and so it was of interest to see what species could actually be detected by ESIMS, and also to assess the effect of the added LiCl medium. Paratungstate B has a more open structure than the previous Keggin species, and so its spectrum is more likely to be complicated by *e.g.* co-ordinated counter ions. Fig. 5(*a*) indeed shows the presence of the highly protonated and lithiated paratungstate B complex ($[H_xLi_yW_{12}O_{42}]^{2-}$, $m/z \approx 1433$, where $x + y = 8$). Some breakdown to monomer and to minor oligomers has occurred, almost certainly in the 15 min since dilution, along with the formation of a W_{10} anion (see below) and some W_{11} species, yet to be identified. However, most of the peaks from *m*/*z* 260 to 600 arise only because an unusually high W, and hence LiCl concentration (10 mmol dm^{-3}), was necessary in order to detect the species with higher mass. As a result, the spectrum shows not only the sodiated species $[NaWO_4]^-$, which commonly arises from the adventitious presence of Na^+ at very low concentrations, but also includes a series of anions of general formula $[(Na\ or\ H)WO_4(LiCl)_n]^-$, hence spaced by 42 mass units. We have observed, by studying alkali-metal halides alone, that such clusters are particularly likely to occur with lithium salts. They put an upper limit on the concentrations that may be used. The W_{12} peak is also extended further to high mass, again probably by added LiCl moieties.

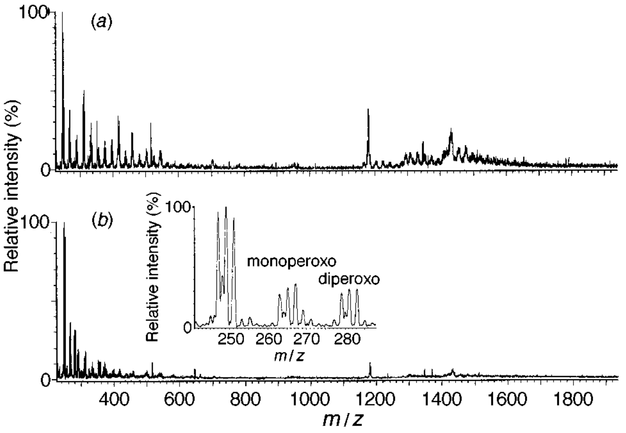

Fig. 5 The ESI mass spectra of (*a*) a pH 6.2 aqueous solution of paratungstate B, 10 mmol dm^{-3} in W, 15 min after dilution from 2 mol dm^{-3} and (*b*) the same solution at 5 mmol dm^{-3} after a reaction time of 45 min with 50 mmol dm^{-3} aqueous H_2O_2

Additionally, a substantial peak, apparently uncomplicated by such clustering, arises at $m/z = 1177$. This could in principle arise from either $[H_2W_{10}O_{32}]^{2-}$ or from $[HW_5O_{16}]^-$. Unfortunately, the isotopic structure of the peak is insufficiently resolved to distinguish these possibilities directly. However, the former species is the well known tungstate Y in its diprotonated state. It can presumably form in response to dilution, and then reach a higher concentration than those of other oligomers because of lower lability. The latter possibility is less likely, because there is no reason to expect a W_5 anion to have reduced lability. Tungstate Y is a comparatively compact anion, with a much lower nominal charge than that of paratungstate B, which may explain why it does not form alkali-metal halide clusters.

Peroxotungstates

To date, only one mass spectrometric study of peroxometalates has been undertaken, which involved the generation of anionic peroxo-molybdenum(VI) and -tungsten(VI) complex ions by means of FAB.[20] The technique involves the sputtering of ions from a glycerol matrix by means of an 8 keV beam of neutral xenon atoms and, therefore, the ions produced are unlikely to reflect those present in solution. However, there is a growing need for a way of detecting peroxometalate anions in aqueous solution. Peroxo complexes of transition metals in solution are sources of active oxygen and many of them may be used as efficient stoichiometric or catalytic oxidants for inorganic and organic substrates.[21–26] In addition, Sastry and Gupta[27] have shown that the preparation of homo- and hetero-nuclear molybdenum(VI) peroxo complexes which contain biologically important amino acids is a facile process. The resulting complexes may have applications in biological studies because of the presence of bioactive metals in association with the peroxo group, although their concentrations are often too low to allow detection by means of NMR or other methods. Even when the concentrations are sufficiently high for ^{183}W NMR spectroscopy, the large variety of peroxo species makes assignment difficult.

The ESI mass spectra reported below show that peroxo spe-

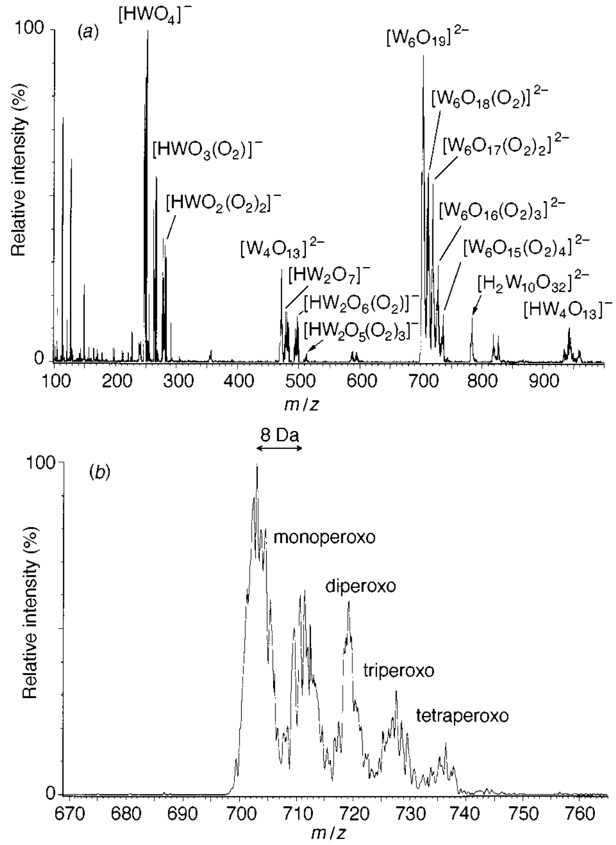

Fig. 6 (*a*) The ESI mass spectrum of a solution of peroxide + tungsten metal, 1 mmol dm^{-3} in W, pH *ca.* 2. The [W$_6$O$_{19}$]$^{2-}$ anion peak is observed in this spectrum and, in addition, the species generated from one to four peroxo substitutions, *i.e.* [W$_6$O$_{18}$(O$_2$)]$^{2-}$, [W$_6$O$_{17}$(O$_2$)$_2$]$^{2-}$, [W$_6$O$_{16}$(O$_2$)$_3$]$^{2-}$ and [W$_6$O$_{15}$(O$_2$)$_4$]$^{2-}$. (*b*) Expansion of the [W$_6$O$_{19}$]$^{2-}$ ion peak and its peroxo analogues which clearly shows the separation of *m*/*z* = 8 between adjacent peaks

cies are indeed readily observable at low concentrations, even in complex mixtures. They are easily identifiable by the shift in mass of the anion due to the replacement of O^{2-} by O$_2$$^{2-}$. The increase in *m*/*z* in the mass spectra arising from one such replacement is 16 for singly charged species and 8 for doubly charged species, and hence both *m* and *z* may be determined independently. The deliberately complex systems chosen for study were (*a*) the reaction of aqueous hydrogen peroxide with powdered tungsten, and (*b*) the known, peroxide-catalysed breakdown of paratungstate B. The products of these reactions are notoriously difficult to characterise.

Peroxide + tungsten metal. The reaction of 30% aqueous H$_2$O$_2$ with powdered tungsten metal has been reported by Kudo *et al.*,[17] although its products have not been fully characterised. Fig. 6(*a*) is the spectrum of a solution approximately 1 mmol dm^{-3} in W, at pH *ca.* 2. It shows that the above reaction unexpectedly generates the [W$_6$O$_{19}$]$^{2-}$ anion, with and without peroxo substitutions. No previous studies have observed the [W$_6$O$_{19}$]$^{2-}$ anion in aqueous solution, although this may have been due to the low sensitivity of other detection methods. The other hexametalate ion peaks reveal up to four successive replacements of O^{2-} by O$_2$$^{2-}$ [Fig. 6(*b*)]. Other species such as [HWO$_4$]$^-$ and [HW$_2$O$_7$]$^-$ are produced in large abundance and the peroxidation (up to two peroxo substitutions) of these species is also evident. In addition, the singly and doubly charged tetratungstate anions [HW$_4$O$_{13}$]$^-$ and [W$_4$O$_{13}$]$^{2-}$ and the doubly charged decatungstate anion [H$_2$W$_{10}$O$_{32}$]$^{2-}$ are also observed in the mass spectrum. Again, only the W$_{10}$ and possibly the W$_1$ species have previously been characterised in aqueous solution. Table 2 summarises the species generated from a range of tungsten solutions and the observed maximum number of oxo replacements by peroxo. Interestingly, the W$_{10}$ anion is not found in a peroxo form, even though the tungstate Y structure is essentially a stretched-out form of the W$_6$ anion.

Table 2 Observed polyoxometalate anions, plus the maximum number of peroxide substitutions occuring upon addition of H$_2$O$_2$

Species	*m*/*z* *	Maximum no. peroxide substitutions observed
[H$_2$W$_{10}$O$_{32}$]$^{2-}$ (or [HW$_5$O$_{16}$]$^-$)	1177	0
[HW$_{10}$O$_{32}$]$^{3-}$	784	0
[W$_6$O$_{19}$]$^{2-}$	704	4
[HW$_6$O$_{19}$]$^-$	1409	4
[W$_5$O$_{16}$]$^{2-}$	588	2
[W$_4$O$_{13}$]$^{2-}$	472	0
[HW$_4$O$_{13}$]$^-$	945	1
[W$_3$O$_{10}$]$^{2-}$	356	1
[W$_2$O$_7$]$^{2-}$	240	2
[HW$_2$O$_7$]$^-$	481	2
[HWO$_4$]$^-$	249	2

* Without peroxo substitution.

Decomposition of polytungstates by peroxide. Fig. 5(*b*) was obtained from the same solution as for Fig. 5(*a*), except that the overall tungsten concentration was reduced to 5 mmol dm^{-3} by the addition of an equal volume of 100 mmol dm^{-3} aqueous H$_2$O$_2$, 45 min before the measurement. Even this two-fold extra dilution noticeably suppresses the LiCl clustering observed previously. At lower mass, [HWO$_4$]$^-$ is also now seen in its mono- and di-peroxo forms. These are the only unambiguous peroxo species detected, in contrast to the previous reaction with tungsten metal. As expected, the intensity of the [H$_x$Li$_y$W$_{12}$O$_{42}$]$^{2-}$ complex is reduced with respect to the three monomer anions. Relatively little hexa- or hepta-metalate forms.

These results together suggest that hydrogen peroxide rapidly attacks the structure of the dodecamer cage, giving mainly monomeric anions which either retain their initial peroxide or else undergo further peroxidation. It also shows that most of the hexametalate ions observed in the previous experiment are formed from the reaction with metal, rather than in some more general way, because they are far less dominant in the present spectrum. Interestingly, there is no clear evidence for intermediate, peroxy oligomers in this case.

Conclusion

The relatively simple spectra of the phosphododecametalate anions show that the ESI process itself does not cause major fragmentation. We have confirmed this in other experiments. Clear evidence for collision-induced dissociation is found only at high cone voltages (>100 V), and even then it is not a dominant process. Thus a W$_n$ species clearly present in the gas phase will also be present in the original aqueous solution. Further investigation will be needed to show how far this remains true for more labile anions. These could conceivably form oligomers rapidly, in the final moments of evaporation, although Figs. 3, 4 and 6 show that this is unlikely to be a significant process with W or Mo.

However, other, more minor modifications of the aqueous anions clearly do take place upon desolvation. There is some tendency for the smaller species to become protonated as they enter the gas phase. Thus [WO$_4$]$^{2-}$, certainly the only species present in dilute, mildly alkaline aqueous solutions, always appears in the gas phase as [HWO$_4$]$^-$. It is likely that the dinegative anion requires solvent water for its stabilisation, and so is forced to accept a proton upon removal of this solvent. The corresponding W$_2$$^-$ anion also appears predominantly, *i.e.*, in its protonated form, although W$_2$$^{2-}$ is also found as a minor component. A dinegative charge predominates for W$_4$ anions and above. As shown in Fig. 4, even a trinegative charge is also possible for a gaseous PM_{12} anion obtained under less acidic conditions.

Fig. 6 and other spectra also show that H_2O may be lost from species that are at least diprotonated in solution, and that metallation by the counter ion is sometimes observed as an alternative to protonation. Added alkali-metal halide clusters are also possible, but may be avoided by using dilute solutions and higher cone voltages. These general observations, plus the variations in concentration inherent to the ESI process, mean that care is required to correlate the mass spectra with the contents of the original solutions. Nevertheless, the ESIMS method is clearly able to detect and identify the types of metalate anions in a solution, even if it cannot precisely define their initial state of protonation or of aquation, and it is also sufficiently quantitative and rapid to permit the tracking of kinetic processes. The results also show that there should be no problem in detecting anions at metal concentrations below 100 μmol dm^{-3}.

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