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^{17}O NMR study of aqueous peroxoisopolymolybdate equilibria at lower peroxide/Mo ratios †

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Aqueous peroxomolybdates have been studied using ^{17}O NMR together with equilibrium measurements and calculations, over a wide range of conditions. Ten peroxo species are identified, mostly in more than one state of protonation. Some are already known in the solid state, or from equilibrium analysis, but structural information is also obtained for $MoO_3(HO_2)^-$ and the new or previously tentative species $Mo_2O_5(O_2)_2^{2-}$, $H_pMo_7O_{23}(O_2)_2^{p-6}$ and $H_pMo_7O_{23}(O_2)^{p-6}$ ($p = 0$–2). Sites of protonation are identified, as are ^{17}O resonances from both bidentate and monodentate peroxide. Several oxygen exchange processes are also seen, including a probable dimer–tetramer exchange.

Introduction

There is rapidly growing interest in aqueous peroxomolybdates as environmentally satisfactory oxidants. For example, they have become of considerable value as replacements for chlorine-based bleaches, in the removal of lignin material from kraft pulp in the paper industry. Peroxomolybdate species so far identified by X-ray crystallography include: $MoO(O_2)_2(H_2O)_2^0$;[1] $Mo_2O_3(O_2)_4(H_2O)_2^{2-}$ and $Mo_2O_2(O_2)_6^{2-}$;[2,3] $Mo_3O_7(O_2)_4^{6-}$;[4] $Mo_4O_{12}(O_2)_2^{4-}$ and $Mo_7O_{22}(O_2)_2^{6-}$;[5,6] $Mo_5O_{10}(O_2)_8^{6-}$;[7] $HMo_7O_{22}(O_2)_2^{5-}$ and $Mo_8O_{24}(O_2)_2(H_2O)_2^{6-}$;[4] $Mo_{10}O_{22}(O_2)_{12}^{8-}$;[8] $Mo(O_2)_4^{2-}$.[9] However, the investigation of other crystalline species has been frustrated by problems of decomposition and of disorder in near-symmetric anions. Also the few existing studies in aqueous solution have been within limited ranges of pH and peroxide concentration, with an emphasis on the use of excess peroxide.[10,11] The speciation when peroxide is not in excess has remained poorly understood. The most incisive methods currently available for a solution study are ^{17}O NMR and potentiometry. Other methods such as Raman spectroscopy and ^{95}Mo NMR offer some information, but are limited by poor resolution of chemically similar species, and by the need for comparatively high concentrations.[10] Even ^{17}O NMR with modest isotopic enhancement requires concentrations that are somewhat above the ideal for correlation with equilibrium calculations at constant ionic strength, as well as being complicated by the effects of chemical exchange, whereas potentiometry is limited by the need to attain chemical equilibrium before any significant decomposition of peroxide has taken place. It is therefore strategic to use firm information from one technique, to resolve uncertainties arising in the other. The present investigation builds on two other studies, one being the preceding paper, using potentiometry, ^{17}O and ^{95}Mo NMR.[10,11] These were made over more limited ranges of concentration and pH, and in the presence of sulfate at 298 and 278 K or chloride at 278 K.[11] Within these ranges, much of the required information can be quantitatively deduced from a few prominent, terminal oxygen resonances. However, other shift regions offer considerable further information, particularly at lower peroxide concentrations, because ^{17}O NMR yields much information even when slow peroxide decomposition cannot be avoided, and particularly so when the identification of the high-peroxo species is already secure. As a result, seven of the above crystallographically known species have now been identified in solution, along with four other previously questionable anions, many new states and sites of protonation and also further kinetic information.

Experimental

The ionic medium was $Na(ClO_4)$ at 25.0 °C, after both sulfate and chloride had been found to coordinate to Mo(VI) at low pH. The studies at lower peroxide/Mo ratio also approximated to the same medium by using 0.300 mol L^{-1} $Na_2(MoO_4)$ solutions, with acidification by small amounts of 11.5 mol L^{-1} $HClO_4$. The temperature in this case was also 25.0 °C, except where lowered for detailed investigation of exchange processes.

Chemicals and analyses

Sodium molybdate dihydrate and perchloric acid (Aldrich, ACS grade) and hydrogen peroxide (May and Baker, 8.9 mol L^{-1}) were used without further purification for the NMR experiments. $H_2{}^{17}O_2$ was kindly supplied by V. Conte, having been prepared from H_2O enriched to 12.3% in ^{17}O by trapping the product of an electric discharge.[12] Enrichment of all other oxygens to 3% was by addition of $H_2{}^{17}O$ (Cambridge Isotope Laboratories). Titrations were carried out so as to minimise the use of isotope. Some titrations were also carried out in the reverse direction, using NaOH, to check for possible hysteresis effects. No evidence for slow processes was found, other than the decomposition of peroxide, and the possible delayed re-equilibration of a minor $Mo_4(peroxo)_2$ species, particularly above pH 7. The decomposition of peroxide did limit the precision of the stoichiometry, because the ^{17}O isotope had to be re-used throughout a series of titrations. However, the peroxide concentration could be checked indirectly in two ways. Titrations were carried out successively towards low and high pH, without any relative loss of species with higher peroxo content, over 8 hours. Furthermore, once the speciation had been substantially established, the bound peroxide content could be also calculated with reasonable accuracy from the

† Electronic supplementary information (ESI) available: concentrations of total Mo, total H_2O_2 and other species expressed as [Mo]. See http://www.rsc.org/suppdata/dt/b2/b206396b/

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oxygen integrals. Also, separate experiments using isotopically enriched peroxide showed directly that free peroxide was not present in significant quantities, below a peroxide/Mo ratio of 2.0. Thus it was possible to calculate meaningful, but not highly accurate equilibrium constants for most species between pH 2 and 7, and to check that some of these were consonant with more accurate measurements at higher peroxide concentration, in closely related media.

NMR spectra

^{17}O NMR spectra were obtained at either 67.8 or 54.2 MHz. Typically, 30,000 transients were collected in 15 min, as this provided adequate time for relaxation. Acoustic ringing reduction sequences were not used, because of the greater importance of leaving the integrals undistorted. The accuracy of the integrals varied strongly with linewidth and overlap, and was rarely better than 20%. However, the actual species concentrations were often more accurate than this, because one anion often gives rise to several peaks in known area ratio. This was particularly valuable in distinguishing the contributions from the diperoxo (per Mo) monomer and dimer anions, because their peaks are broadened by exchange at pH > 2, and their terminal oxo resonances are only 1 ppm apart. All species present as >2% of total Mo should have been detected by the ^{17}O measurements, unless their resonances are severely broadened.

Equilibrium calculations at lower peroxide concentrations

The two largest sets of 298 K titration data were selected for equilibrium calculations. They respectively used 65 and 380 mmol L^{-1} peroxide, and both had 300 mmol L^{-1} $[Mo]_{total}$ and no additional ionic medium. Data at other temperatures and concentrations were used for clarification, and as qualitative indicators of the number of molybdenum atoms per anion. The initial calculations, as with studies in different media, used LAKE.[13] Equilibrium constants were fitted to the data, first at the lower peroxide concentration, where the Mo_7X_n species dominate, and then at the higher ratio. The constants for the dominant anions became the starting values for more complete fits, involving a wider range of species, but in these cases the data were not of sufficient precision to extend automated fitting reliably to the more minor species. Therefore the subsequent calculations involved visual fitting of a more complete equilibrium model to the data, supported by ^{17}O NMR data obtained at other concentrations and temperatures.

Results

Anion formulas are only given below in their full form when the structure is reasonably certain, and even in these cases the possibility remains that an additional coordinated water molecule has left no spectroscopic signature. The more ambiguous formulas are given in a short form, such as MoX_2^{2-}, where X = coordinated peroxide. The charge is omitted when more than one protonation state is implied.

The preceding 298 K measurements at 5–20 mmol L^{-1} in 300 mmol L^{-1} Na_2SO_4 medium and at high peroxide (X)/Mo ratio used potentiometry, ^{95}Mo and terminal oxo ^{17}O resonances to identify the anions MoX_2^-, MoX_2 (pK_a 2.16), MoX_2S^{2-}, MoX_2S^- (pK_a 1.00), $Mo_2X_4^{2-}$ and Mo_7X^{6-} through to Mo_7X^{3-} (pK_a 5.29, 3.74, 2.49), in the pH range 2–5, from potentiometry alone.[10,11] They also identified more minor MoX^- and MoX species (pK_a 2.69) from potentiometry alone and left open the possibility of a parallel $Mo_7X_2^{n-}$ series, of other anions being present, especially at higher concentrations of Mo and peroxide, and of transient tri- and tetraperoxo monomers. A further study at 278 K and at high peroxide ratio has also identified a $Mo_2X_6^{2-}$ dimer and, in chloride medium, a MoX_2Cl^- monomer. Most of these conclusions are verified and extended by the present NMR measurements, made over a wider range of pH and peroxide concentration, in perchlorate medium. More detailed formulae for the species are discussed below.

High peroxide ratios

Fig. 1 shows all the peroxomolybdate resonances in a typical

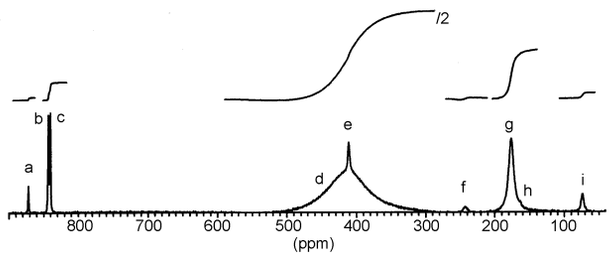

Fig. 1 67.8 MHz ^{17}O NMR spectrum, 300 mmol L^{-1} Mo in D_2O, H_2O_2/Mo = 2.6, 3% isotopic enrichment, pH 2.4 following acidification with H_2SO_4, 298 K. Peak assignments using simplified formulae, with charges omitted: a MoX_2S (=O); b MoX_2 (=O); c Mo_2X_4 (=O); d (broad peak) bound bidentate peroxide; e (narrower peak) Mo_2X_6-bound monodentate peroxide; f Mo_2X_4 (–O–); g free peroxide; h (shoulder) sulfate; i MoX_2 (–OH).

high-peroxo ^{17}O NMR spectrum at pH 2.4, with 300 mmol L^{-1} Mo and a ratio H_2O_2/Mo = 2.6. This spectrum is also partially discussed in the preceding paper, but illustrates several further points here.[11] The peroxide was also enriched to 12.3 % ^{17}O. Sulfuric acid was used to acidify the original molybdate in this case, and the oxygens of the bound sulfate give rise to a small shoulder on the right of the 176 ppm peak. Peroxide gives the two broad peaks at 176 and *ca.* 411 ppm, along with a smaller and much narrower resonance superimposed on the broadest one. The two peaks at 411 ppm arise from bound peroxide, and the 176 ppm peak is from free peroxide.[11] The other resonances arise from oxo ligands, with 3% isotopic enrichment. Because their shifts and intensities depend markedly on pH and concentration, they may be assigned unambiguously as follows, using the shorthand formulae as above: MoX_2S^{2-} at 872 ppm; MoX_2^- at 843.2 (1O) and 73.8 (1O) ppm; $Mo_2X_4^{2-}$ at 840.4 (2O) and 243 (1O) ppm. In each case, at this pH, there is some admixture of the corresponding protonated species. The pK_a values in this medium, derived from the Henderson–Hasselbalch equation fitted to the NMR data alone are listed below in Table 1, for comparison with the present perchlorate medium. There is no direct evidence in either medium for any further bound water ligands, but these might still be present, in rapid exchange with the solvent (see below).

Several of the line widths also depend markedly upon pH and temperature. The terminal O peaks are discussed in the preceding paper.[11] Also the MoX_2^- peak around 74 ppm shifts to 99 ppm when the pH exceeds 3.5, and broadens into invisibility above pH 7.5. The corresponding spectra obtained at 278 K generally show narrower resonances, and also reveal two further species. A very broad peak emerges at 643.7 ppm (298 K shift) and pH > 4. It then narrows without further shifting as the pH increases, and indeed also becomes visible at room temperature if pH > 4.5. The calculations below imply that its resonance would also be apparent in Fig. 1, if it were not so greatly broadened. Its dependence on pH and concentration is consistent with assignment to the monoperoxo anion MoX^-, proposed from potentiometry alone in the earlier study.[10]

A further complexity arises as the pH is raised above 5.5. At 278 K, the $Mo_2X_4^{2-}$ peak for bridging oxygen that appears at 243 ppm in Fig. 1 splits into two components. Clearly an exchange process has been slowed. One peak starts to decrease in shift above pH 7, as shown in Fig. 2, while both peaks become insignificant above pH 8.5. The corresponding resonance at

Table 1 A comparison of aqueous peroxoisopolymolybdate properties

Anion[a]	δ_O	Log β[b]	pK_a[c]	Log β[d,e]	pK_a
$[HMoO_2X_2]^-$	831.1(1O), 98.9(1O)	11.5			
	834.1[d]			11.61[d]	
$[H_2MoO_2X_2]$	871.4 (1O), 9.5(1O)	13.54	2.04 (0.10)		
	873.8[d]			13.70 (0.05)[d]	2.09[d]
$[Mo_2O_3X_4]^{2-}$[e]	831.1(2O), 314.7(1O)	23.9			
	832.9[d]			23.77 (0.11)[d]	
$[HMo_2O_3X_4]^-$[e]	871.4(2O), 62.5(1O)	25.9	2.0		
$[HMoO_3X]^-$	643.7	8.7		8.53[d]	
$[Mo_2O_5X_2]^{2-}$	853 (4O), 317 (1O)	18.2			
$[Mo_4O_{12}X_2]^{4-}$	789.5(8O), 351(4O)	26.8[f]			
$[HMo_4O_9X_4]^-$	879 region	48.8[f]	1.7		
$[Mo_7O_{23}X]^{6-}$	a:124.3 aO:151.5 b:356.8 b′:397.6 cO:344.3 c′:818.4 dO:848.2 e:798.2 eO:700.7 f:793	56.48		56.71 (0.11)[g]	
$[HMo_7O_{23}X]^{5-}$	a:123 aO:160 b:352 b′:389 cO:306 c′:834 dO:865 e:816 eO:709 f:833	60.88	4.4	62.00 (0.07)[g]	5.29
$[H_2Mo_7O_{23}X]^{4-}$	a:127 aO:168 b:347 b′:377 cO:257 c′:849 dO:877.0 e:821 eO:714 f:842	64.48	3.6	65.74 (0.06)[g]	3.74
$[H_3Mo_7O_{23}X]^{3-}$	[h]	66.28[h]	1.8[h]	68.23[h]	2.49[h]
$[Mo_7O_{22}X_2]^{6-}$	aO:151.5 b:379.2 b′:398.4 cO:344.3 c′:818.4 dO:843.6 eO:740.0 f:793	59.3			
$[HMo_7O_{22}X_2]^{5-}$	aO:160 b:381 b′:378 cO:306 c′:834 dO:860 eO:750 f:833	63.7	4.4		
$[H_2Mo_7O_{22}X_2]^{4-}$	aO:168 b:385 b′:391 cO:257 c′:849 dO:875 eO:759 f:842	67.5	3.8		
$[H_3Mo_7O_{22}X_2]^{3-}$	[h]	71.0	3.5		

[a] $X^{2-} = (O_2)^{2-}$, $S^{2-} = (SO_4)^{2-}$. [b] Log (formation constant) from $[MoO_4]^{2-}$, H^+ and H_2O_2. [c] Self-medium with $[Mo]_{total}$ = 300 mmol L^{-1}, 298 K. [d] 300 mmol L^{-1} $Na_2(SO_4)$ medium, 278 K. Measurements on oxo peak only. [e] Two isomeric species – see text. [f] Very approximate – see text. [g] As d but 298 K potentiometric data from ref. 11, where Mo_7X_2 is not included in the model. [h] Not reliable, as pK_{a3} is just outside the pH range.

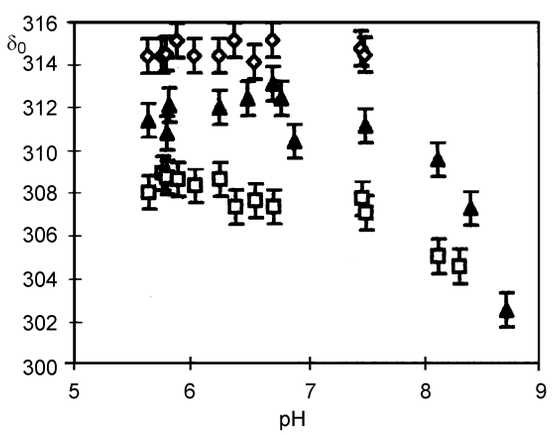

Fig. 2 ^{17}O shifts *vs.* pH for –O– resonances of Mo_2X_4. ◇ dimer with single oxo bridge, 273 K; ▲ combined peaks, 298 K; □ dimer with double oxo bridge, 273 K.

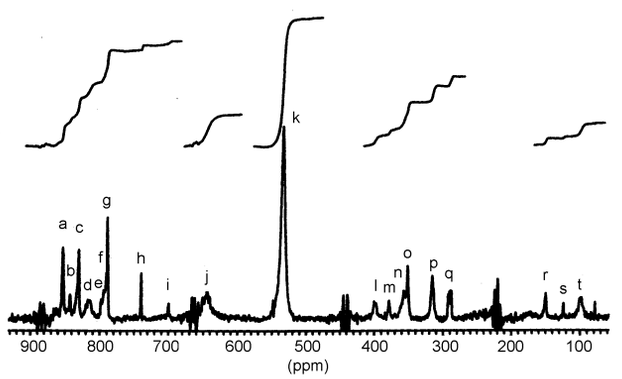

Fig. 3 54.2 MHz ^{17}O NMR spectrum, 300 mmol L^{-1} Mo in D_2O, H_2O_2/Mo = 0.66, 3% isotopic enrichment, pH 6.1: a Mo_2X_2 (=O); b **dO** (all such letter assignments refer to Mo_7X_2 unless otherwise noted, although minor contributions from Mo_7X are often also present at almost the same shift); c MoX_2 + Mo_2X_4 (=O); d **c′**; e **e**(Mo_7X); f **f**; g Mo_4X_2 (=O); h **eO**; i eO(Mo_7X); j MoX; k Mo; l **b′**; m **b**; n **b**(Mo_7X) + **c**; o Mo_4X_2 (–O–); p Mo_2X_4 + Mo_2X_2(–O–); q ClO_4^- (natural abundance); r **aO**; s **a**(Mo_7X); t MoX_2 (OH).

high shift (843 ppm in Fig. 1) is not detectably affected in the same way, presumably because the corresponding resonances from each component species have very similar chemical shifts.

No other species were detected at 298 K even when excess peroxide was present, apart from two transient anions. The rapid addition of excess peroxide to molybdate, giving a solution at pH *ca.* 8, produces a resonance at 589.7 ppm that persists for about 15 min at 298 K. This is not the Mo_2X_6 dimer[11] found at 841 ppm and 278 K but it could arise from a monomeric triperoxo species, MoX_3^{2-}. An even more transient orange color is also seen immediately upon addition of peroxide at pH > 7, lasting for about 10 s. It gives no detectable oxo resonance, but could arise from MoX_4^{2-}.[9]

Low peroxide ratios

Many different resonances appear when peroxide/Mo < 2, quite apart from heptamolybdate peaks. Most of them can be seen in the Fig. 3 spectrum. Their shifts are listed in Table 1 and their pH stability ranges are illustrated by the points in Fig. 4, along with those of the species described above. Individual species are now discussed.

MoO_4^{2-} (δ_O = 533.3)

This well-established resonance appears at all pH values down to 5, and especially at high pH.[14] At 298 K it is markedly broad, especially below pH 5.5 and at the higher peroxide concentrations, although it narrows by a factor of *ca.* 6 at 273 K. There is no variation of shift with pH, and δ_O is entirely consistent with tetrahedral coordination, according to an earlier correlation of bond order with oxygen shift.[15,16]

$MoO_3(HO_2)^-$ (δ_O = 643.7)

This 'MoX$^-$' peak appears consistently at lower peroxide concentrations, between pH 7.5 and 4.5. At lower pH values it is too broad to be detected in the spectra. It also narrows on cooling, as for MoO_4^{2-}, although the corresponding temperature factor is now only 3. These different variations in linewidth are not consistent with a simple process of mutual oxygen exchange. They also depend on pH in the opposite way to the $MoO(OH)(O_2)_2^-$ (MoX_2^-) resonance described above. They probably each arise from oxygen exchange with the

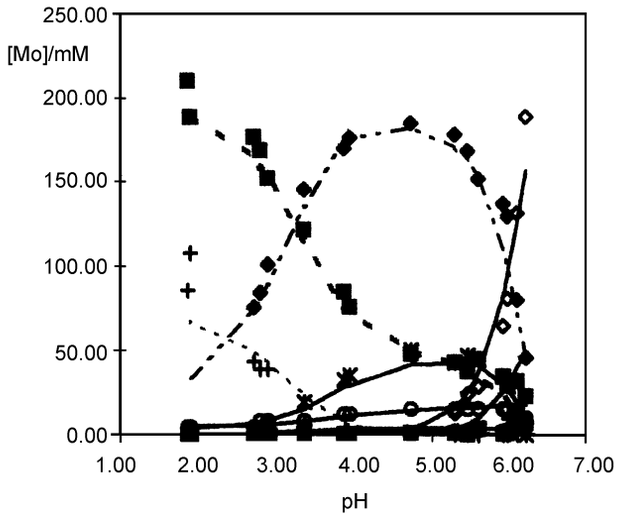

Fig. 4 Calculated (lines) and observed (points) concentrations of species, as [Mo] *vs.* pH. 298 K. [Mo] total = 300 mmol L^{-1}, peroxide: Mo = 0.22. Predominant species are: ■ and broad dash line, Mo_7X_2; ◆ and dash–dot line, Mo_7X; + and dotted line, Mo_8; * and solid line, Mo_7; ○ and unbroken line, MoX; ◇ and unbroken line, Mo.

solvent. An associative mechanism is likely for tetrahedral anions. The Mo^{2-} and MoX^- oxo resonances also lie outside the normal range for 5- or 6-coordinate Mo–O, but are both approximately consistent with the average bond order expected for tetrahedral coordination.[16] MoX^- gives just one oxo oxygen resonance, implying either rapid H exchange or else protonation at end-on peroxide. This observation contrasts with the hexa- or heptacoordinate anion MoX_2^{2-}, which gives two oxo resonances of equal area. The breadth of the MoX^- resonance below pH 4.5 means that the NMR evidence can neither confirm nor disprove the pK_a of 2.70 proposed previously for this anion.[10] Fig. 3 of ref. 10 shows that the corresponding ^{95}Mo resonance also differs from that of MoX_2^- by being substantially narrower, again as expected for tetrahedrally coordinate Mo(VI). The present ^{17}O NMR data serve to confirm the existence of a species that was previously open to dispute.

$Mo_4O_{12}(O_2)_2^{4-}$ [δ_O = 789.5 (8O) and 351 (4O)]

This relatively minor anion has only two resonances, of constant width and with a 2 : 1 area ratio over the stability range, pH 4.5 to 8. Their areas depend on Mo and peroxide concentration consistently with the above formula. The optimum pH for formation is 6. However, there is some evidence that this anion decomposes unusually slowly at the high pH end of its range. Therefore its state of protonation, discussed below, cannot be reliably determined by measurements that assume chemical equilibrium.

$Mo_2O_5(O_2)_2^{2-}$ [δ_O = 853 (4O) and 317 (1O)]

This cautiously suggested formulation is supported by equilibrium calculations and by other observations of how the 853 ppm peak area depends on the concentrations of Mo and peroxide, including spectra using only 80 mmol L^{-1} Mo. The species, like MoX^-, is stable between pH 4.5 and 8. The weak bridging O resonance of this $Mo_2X_2^{2-}$ species at 317 ppm is generally overlapped by the corresponding resonance of $Mo_2X_4^{2-}$ at 315 ppm, but it appears without this overlap at low peroxide concentration. Its contribution to the area of the combined peak is also consistent with the anticipated 4 : 1 area ratio.

$HMo_4O_9(O_2)_4^-$ (δ_O = 879 *etc.*)

A broad resonance appears at 879 ppm, below pH 3.5, with a second broad component at 855 ppm underlying the MoX_2^- oxo peak at low pH. It is tentatively given the above formula on the basis of equilibrium calculations, but may in fact be a mixture of relatively condensed species, as would be anticipated under these conditions. As with all the other anions listed in this section, it is destroyed by excess peroxide.

Heptamolybdate species

The accepted scheme for labeling the oxygens in Mo_7 is shown in Fig. 5g and 5h. The peroxo-substituted ends of Mo_7X and

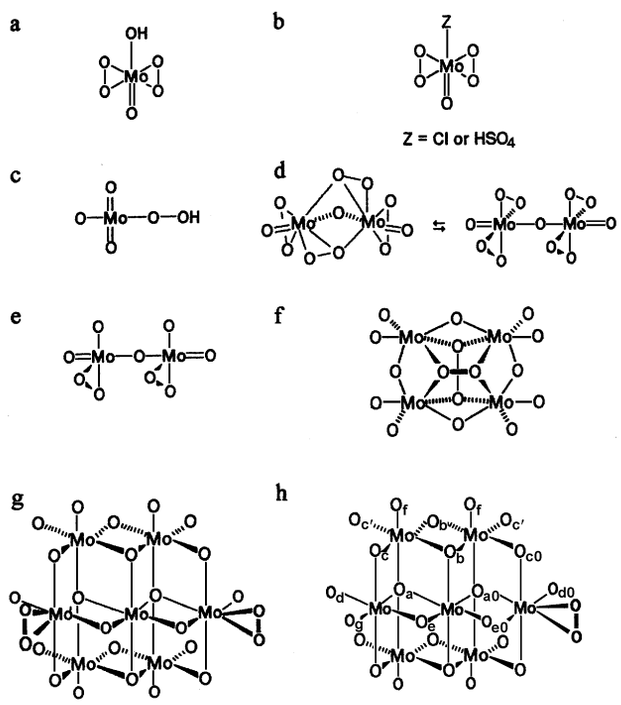

Fig. 5 Schematic, proposed structures of major species: a MoX_2^- (omitting a possible coordinated H_2O); b MoX_2Z^- (Z = Cl or HSO_4^-); c MoX^-; d $Mo_2X_4^{2-}$ (two isomers); e $Mo_2X_2^{2-}$; f $Mo_4X_2^{4-}$; g $Mo_7X_2^{6-}$; h Mo_7X^{6-}.

Mo_7X_2 are identified below by an added **O** label, with a final **1** or **2** to distinguish Mo_7X from Mo_7X_2 where possible. Although peaks from heptamolybdate species show only weakly in Fig. 1, they dominate the corresponding spectra in the range [peroxide]/[Mo] = 0.2–0.7. Some of the oxygen resonances, such as **dO** and **eO**, are narrow and are essentially free from overlaps, so that the Mo_7, Mo_7X and Mo_7X_2 species can readily be quantitated over the full pH range. This assists the assignment of the other heptamolybdate peaks. Fig. 6 shows that all the heptamolybdate species have shifts that depend markedly on pH, with protonation occurring predominantly at the **cO** resonances in Mo_7X and Mo_7X_2. This contrasts with Mo_7, where protonation occurs mainly at the **b** and **b′** oxygens.[17]

Previous work on Mo_7 has shown that the **c**, **g** and **d** oxygen resonances are severely broadened at room temperature by an internal exchange process.[14] This broadening also takes place at the unsubstituted end of Mo_7X. However it is not seen at the peroxo-substituted ends, even at elevated temperature. The **cO** and **dO** peaks are readily detected, and the absence of any **gO** peaks proves that substitution has taken place solely at the **g** sites. This has already been demonstrated crystallographically for Mo_7X_2, but Mo_7X has previously been tentatively detected only by potentiometry and ^{95}Mo NMR.[10,11] The changes in shift upon peroxo substitution are fully consistent with the above, and no other site of substitution is found.

The pK_a values for Mo_7X and Mo_7X_2 are too closely spaced to be calculable from the data in Fig. 6. However, they can be deduced from equilibrium calculations, as discussed below. The shifts for the acidified heptamolybdates in Table 1 rely on this

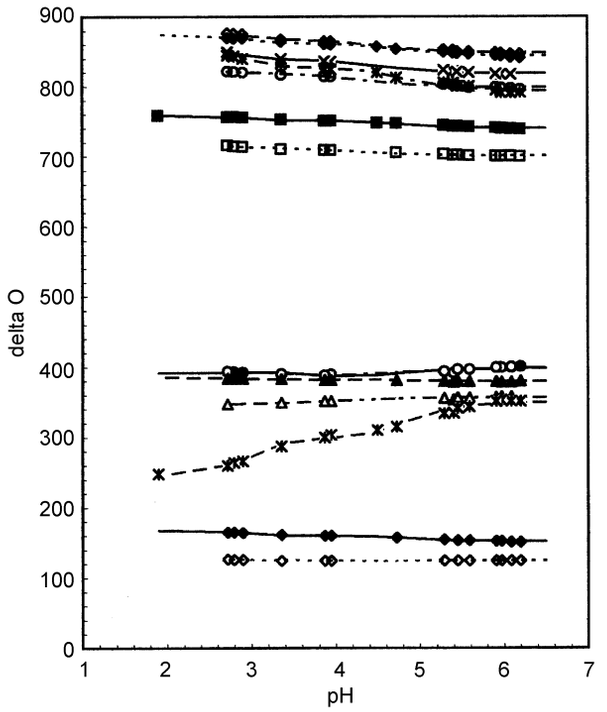

Fig. 6 $Mo_7X_2^{6-}$ and Mo_7X^{6-} oxygen shifts *vs.* pH. Labels as Fig. 5h with added numerals to distinguish X_1 from X_2, in descending shift order: **dO1**; **dO2**; **c′**; **e1**; + **f**; **eO2**; **eO1**; **b′1**; **b′2**; **b2**; **b1**; + **cO2**; **aO**; **a**.

information, and are therefore less accurate than those for the hexanegative anion.

In addition to the above heptamolybdates, the non-peroxo-Mo_7 anion was also seen at peroxide/Mo ratios below 0.25, and was replaced by (non-peroxo) octamolybdate below pH = 3.4. Octamolybdate has previously only been detected in a Li^+ medium.[17] However, no Mo_8X_n anions were detected.

Equilibrium calculations

The LAKE program[13] was first applied to the data obtained with 65 mmol L^{-1} peroxide, because several of the equilibrium constants were known approximately from the earlier studies, and thus made reliable starting points for the data-fitting process.[10,11] The pH range was initially restricted to 3.8–6.0, where most of the species present in this range were readily identifiable from their oxygen shifts. It was then extended to include data down to pH = 1.8, and then further extended to data from solutions 380 mmol L^{-1} in peroxide. However, as described above, final manual fitting to the data was also necessary, because the concentration measurements for the minor species were insufficiently accurate for fully automated fitting.

The resulting fits are shown in Fig. 4 (65 mmol L^{-1} peroxide, 300 mmol L^{-1} Mo) and 7 (380 mmol L^{-1} peroxide, 300 mmol L^{-1} Mo). Although not perfect, particularly at the extremes of pH, they unambiguously settle the formulation of most of the anions present. The calculated β values (log formation constants from MoO_4^{2-}, H^+ and H_2O_2) are given in Table 1. The results of the calculation were also qualitatively consistent with data obtained at different concentrations; $[Mo]_{total}$ was in fact varied between 80 and 600 mmol L^{-1}, but these data were not included in the computer fits because it was not feasible to control ionic strength at these extremes. The equilibrium constants are also in good agreement with earlier measurements (Table 1) in each case where these are available.[11] The calculations predict that when the peroxide to Mo ratio is only slightly greater than 2, the only significant species present between pH 3 and 6 are MoX_2^- and $Mo_2X_4^{2-}$. With $[Mo]_{total}$ = 300 mmol L^{-1} and with perchlorate as counterion, the contributions to $[Mo]_{total}$ from each species are predicted to be almost equal. Experiment confirms this.

Discussion

The NMR spectra are very largely consistent with the known crystal structures, although some of these structures seem to be confined to the solid state. The spectra also reveal several new species, and illuminate the thermodynamics and kinetics of their equilibria. Individual structures are now discussed.

Monomeric species

$MoO(OH)(O_2)_2^-$ and $MoO(OH_2)_2(O_2)_2^0$. The neutral species was shown by Shoemaker *et al.* to be pentagonal bipyramidal, with two bidentate peroxo ligands and one water (Mo–O = 2.084 Å) in the plane, and the other water (Mo–O = 2.325 Å) and the oxo ligand (Mo–O = 1.647 Å) approximately axial.[1] In solution, one of the water ligands is not seen, with either charge state, and so is presumably either lost or in rapid exchange with solvent. We prefer the former explanation for the neutral species (pK_a = 2.04), as the other water ligand is clearly visible down at the lowest pH values used (9.5 ppm at pH = *ca.* 1.7) and retains an area equal to that of the oxo resonance. It would otherwise be hard to explain why only one of the two waters should exchange rapidly. However, only exchange can explain the data for the monoanion. In this case the new OH peak appears at 98.5 ppm. This is a fairly low but not unreasonable shift for a bound OH. As expected, there is a corresponding, modest decrease in the shift of the oxo ligand. The rate of proton transfer from the hydroxo to the oxo ligand is far slower than the oxo–hydroxo exchange in HVO_4^{2-} and therefore we propose the structure in Fig. 5a, which offers a steric barrier to this exchange.[18] The presence of the bound water is supported by preliminary EXAFS measurements. The broadening at pH > 7.5, with no significant shift, probably implies a $MoO_2(O_2)_2^{2-}$ species acting as a more symmetrical transition state for H exchange, but having a pK_a >> 7.5. For completeness, Fig. 5b also shows the proposed structures for the corresponding sulfato and chloro species reported in the preceding paper. For these there is no evidence for additional bound water.

$MoO_3(HO_2)^-$. Reasons are given above for the tetrahedral structure proposed in Fig. 5c, with end-on hydroperoxide coordination giving tetrahedral Mo. There is a precedent for Mo(VI) to bind to hydroperoxide end-on.[2] As there is evidence from equilibrium calculations for a $MoO_2(OH)(HO_2)^0$ species below pH 2.70, the exchange process that broadens only the oxo peak below pH 4.5 may involve the exchange of OH^- with solvent water.[11]

Dimeric species

$H_3Mo_2O_4(O_2)_4^-$, $H_2Mo_2O_4(O_2)_4^{2-}$ and $HMo_2O_4(O_2)_4^{3-}$. As $Mo_2X_4^{2-}$ is in slowish exchange with MoX_2^-, it is reasonable to expect a simple dimeric structure as on the right of Fig. 5d. This is essentially the structure of Le Carpentier *et al.*, though the bound waters have been provisionally omitted because no corresponding oxygen resonance is seen.[3] We identify the second proposed structure either as a dimer with additional peroxo bridges, possibly as proposed in Fig. 5b (left) or as a symmetrical tetramer, such as one recently identified crystallographically by Hashimoto *et al.*, having two bridging oxygens and four bridging peroxo ligands.[19] These proposals fit the observation that the integrals show no relative loss of bridging oxo, even though the two exchanging structures are in comparable proportions, and also because Hashimoto's simultaneously present dimer and tetramer have structures that would permit mutual exchange *via* the facile breaking of peroxo bridges, and would also permit the coexistence of a peroxo-bridged dimer. The separation of the dimers' bridging oxo resonances is only

resolvable at pH > 6 and 278 K. Fig. 2 shows that the two oxo shifts at pH 6.5 are at 314.4 and 308.2 ppm. Above pH 7 the 314.4 ppm peak disappears but the 308.2 ppm peak moves to lower shift. There is no detectable splitting in the terminal oxo resonance. We propose that deprotonation destroys the dimer structure with its single oxo bridge, but simply replaces one of the two oxo bridges in the tetramer by OH and O, or alternatively removes the oxo bridge in the Fig. 5d (left) structure.

At low pH the shift of the bridging oxygen drops from 314.7 to 62.5 ppm with no loss of relative area, implying protonation at the bridging oxygen in both species.

$Mo_2O_5(O_2)_2^{2-}$. The two peaks corresponding to this dimer are weaker than those for $Mo_2X_4^{2-}$, but by no more than expected from the relative ratio of MoX_2^- to MoX^-. They become somewhat more prominent at lower [Mo] and [H_2O_2]. The shifts are also similar to $Mo_2X_4^{2-}$, so we propose the simple structure in Fig. 5e, with a single oxo bridge. This anion has not been reported previously, apart from a very early and tentative suggestion. It was too minor to be found by potentiometry.

The $Mo_2X_6^{2-}$ anion was not seen at the lower peroxide concentrations used here.

Tetrameric species

$Mo_4O_{12}(O_2)_2^{4-}$. The clear ^{17}O NMR signature of this anion is two peaks, unaffected by pH or exchange. Their shifts and 2 : 1 terminal : bridging ratio fit nicely with the structure in Fig. 5f, first identified by Stomberg *et al.*,[5] but the concentration *vs.* pH data in Fig. 7 are less clear. The resonances are found over a

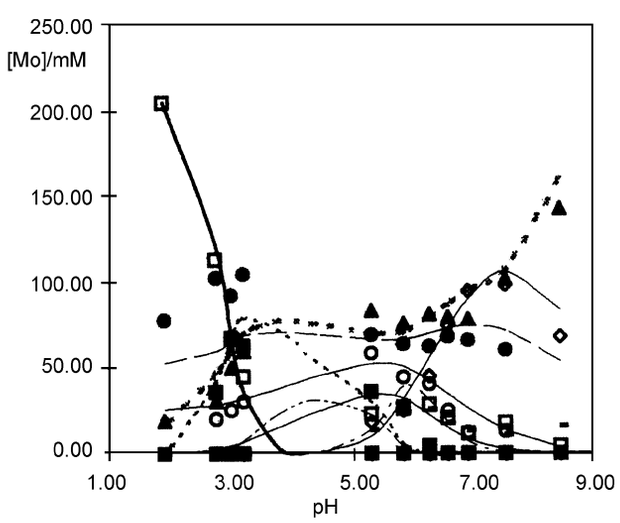

Fig. 7 Calculated (lines) and observed (points) concentrations of species, as [Mo] *vs.* pH. 298 K, $[Mo]_{total}$ = 300 mmol L^{-1}, peroxide: Mo = 1.27. Predominant species are: □ and solid line, Mo_4X_4 (pH 2–3), □ and dash–dot line, Mo_2X_2 (pH 4–9); ● and narrow dash line, MoX_2; ▲ and broad dash line, Mo_2X_4; ■ and dot line, Mo_7X_2; – and unbroken line, Mo_4X_2; ○ and unbroken line, MoX; ◇ and unbroken line, Mo.

wider pH range than is possible for a single Mo_4 anion, and the pH of their maximum intensity is more consistent with the formulation $HMo_4O_{13}(O_2)_2^{5-}$. Unfortunately, Stomberg's structure has no hydrogens, and any addition of OH^- would destroy its considerable symmetry. We therefore propose that the observed anion is kinetically rather than thermodynamically stable at pH > 6, on a timescale faster that the limiting timescale of peroxide decomposition. If this is true, then the equilibrium calculations will not be reliable for it. The same partial limitation may also possibly apply to the equilibrium data for $Mo_2O_5(O_2)_2^{2-}$.

$HMo_4O_9(O_2)_4^-$. This species dominates at low pH and at a 1 : 1 Mo : peroxide ratio, although it is only identifiable in the spectra as broad, overlapped terminal oxo resonances, whose shift depends slightly on pH. It was therefore not possible to identify any structure, and indeed it may be a mixture of species. The above $Mo_4X_4^-$ formula fits the integral data in Fig. 7, and thus enables the other species to be fitted at pH < 3, but is otherwise only nominal. The difficulty of quantifying this resonance may explain the poorer fits below pH 3, in Fig. 7. The available data fit best to the calculation if a protonated species with pK_a of 1.7 is included. The data do not fit well to the diperoxo octamer reported by Stomberg *et al.*[4]

Heptameric species

$Mo_7O_{23}(O_2)^{6-}$ and $Mo_7O_{22}(O_2)_2^{6-}$. These two peroxoheptamolybdates are unambiguously identified and distinguished by their narrower resonances. $Mo_7X_2^{6-}$ is clearly the anion identified by Stomberg *et al.*,[5,6] with the structure shown schematically in Fig. 5g, whereas Mo_7X^{6-} (Fig. 5h) has so far only been detected tentatively by potentiometry, because of the difficulty of distinguishing it from $Mo_7X_2^{6-}$.[11] The ^{17}O chemical shifts of Mo_7X^{6-} at the non-peroxo end of the anion are very similar to those in Mo_7^{6-}, as expected, and are also similar to $Mo_7X_2^{6-}$ at the other end.[17] Thus the structure is well defined.

All the substitution sites for both $Mo_7X_2^{6-}$ and Mo_7X^{6-} are clearly at position **g**. The main changes in shift when peroxide replaces O at **g** are that δ_O increases for the neighboring oxygens **dO** and **eO**, with a concomitant drop at **e**. The bonds to peroxide will inevitably be longer than to **g** in the original Mo_7 anion, and so one expects other Mo–O bonds in the same coordination sphere to shorten. This is confirmed for $Mo_7X_2^{6-}$ by the X-ray data, and for either peroxoheptamolybdate by the changes in shift, because any increase in δ_O always correlates closely with shortening of the corresponding Mo–O bond.[16] The **c**–**d**–**g** exchange process previously reported in Mo_7^{6-} will inevitably be quenched by peroxide substitution at **g**, because these oxygens exchange by the rotation of a transient, tetrahedral-$MoO_cO_dO_g$ moiety. The present data confirm this.[14]

$H_nMo_7O_{23}(O_2)^{(6-n)-}$ and $H_nMo_7O_{22}(O_2)_2^{(6-n)-}$. Stomberg *et al.* proposed in a preliminary report that $Mo_7X_2^{6-}$ protonates at **cO**.[4] NMR confirms this for each protonation step, in either peroxoheptamolybdate. The pK_a values are similar, although hard to determine precisely. As is usually observed, the shifts of the other oxygens rise somewhat as **cO** protonates. The ratio [Mo_7X_2] / [Mo_7X] rises markedly at lower pH values, and this is most easily explained by a higher third pK_a step, presumably made possible by the presence of a second peroxo-substituted site.

Octameric species

The spectra at low peroxide ratio clearly show the spectroscopic signatures of $Mo_8O_{26}^{4-}$ below pH 4. This is surprising, because aqueous octamolybdate has only been reported previously as its lithium salt.[17] However, as noted above, there is no clear evidence for any peroxo-substituted octamolybdate species in solution.

Chemical shifts

The ^{17}O chemical shifts are all consistent with the previously noted inverse correlation with metal-to-oxygen distances, where these are known or can be estimated credibly.[16] When any of the above species is protonated, the bridging O or OH is substantially lowered in chemical shift, whilst the corresponding terminal oxygens increase in shift by a smaller amount, as expected on electrostatic grounds.

Conclusions

This study offers a broad, semiquantitative view of the aqueous chemistry of peroxomolybdates, at least above pH 2,

and so allows comparison with that of isopolymolybdates. The general effects of adding peroxide to aqueous molybdates are to slow some exchange processes and to limit condensation, particularly at higher peroxide concentrations. The ^{17}O NMR resonances of peroxomolybdates are generally sharper than for the corresponding molybdates.[17] The only peroxomolybdate exchange processes that were detectable *via* broadened terminal O peaks were water exchange between MoX and bulk water, the same between MoX_2 and bulk water, and that between MoX_2^- and $Mo_2X_4^{2-}$ (either isomer). This may be because peroxide, as a bidentate ligand, inhibits associative transition states. Also, its greater bulk probably inhibits the formation of oligomers. Indeed, when the peroxide : Mo ratio exceeds 2, condensation goes no further than the dimer, even at low pH. This may be compared with aqueous vanadate, where the addition of even lower amounts of peroxide completely prevents the formation of decavanadate and of other oligomers, although it does similarly give rise to a range of peroxovanadate dimers.[20]

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References

1 C. B. Shoemaker, D. P. Shoemaker, L. V. McAfee and C. W. DeKock, *Acta Crystallogr., Sect. C*, 1985, **41**, 347–350.
2 R. Stomberg, *Acta Chem. Scand.*, 1968, **22**, 1076–1090.
3 J.-M. Le Carpentier, A. Mitchler and R. Weiss, *Acta Crystallogr., Sect. B*, 1972, **28**, 1288–1298.
4 L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1981, **35**, 823–825.
5 R. Stomberg, L. Trysberg and I. Larking, *Acta Chem. Scand.*, 1970, **24**, 2678–2679.
6 I. Persdotter, L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 335–343.
7 I. Persdotter, L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 1–7.
8 I. Persdotter, L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 83–90.
9 R. Stomberg, *Acta Chem. Scand.*, 1969, **23**, 2755–2763.
10 F. Taube, M. Hashimoto, I. Andersson and L. Pettersson, *J. Chem. Soc., Dalton Trans.*, 2002, 1002–1008.
11 F. Taube, I. Andersson, I. Toth, A. Bodor, O. Howarth and L. Pettersson, *J. Chem. Soc., Dalton Trans.*, 2002, 4451–4456.
12 V. Conte, G. Miozzo and R. Salmaso, *Chim. Oggi*, 1989, **7**, 31.
13 N. Ingri, I. Andersson, L. Pettersson, A. Yagasaki, L. Andersson and K. Holmström, *Acta Chem. Scand.*, 1996, **50**, 717–734.
14 O. W. Howarth and P. Kelly, *J. Chem. Soc., Chem. Commun.*, 1988, 1236–1238.
15 E. Heath and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1981, 1105–1109.
16 O. W. Howarth, in *Polyoxometallates: From Platonic Solids to Antiretroviral Activity*, ed. M. J. Pope and A. Müller, Kluwer, Amsterdam, 1993, pp. 167–176.
17 O. W. Howarth, P. Kelly and L. Pettersson, *J. Chem. Soc., Dalton Trans.*, 1990, 81–84.
18 O. W. Howarth, I. Andersson, J. J. Hastings and L. Pettersson, *J. Chem. Soc., Dalton Trans.*, 1996, 3357–3361.
19 M. Hashimoto, presented in part at the 9th Nordic Symposium on Coordination Chemistry, Umeå, June, 2002.
20 I. Andersson, S. Angus-Dunne, O. W. Howarth and L. Pettersson, *J. Inorg. Biochem.*, 2000, **80**, 51–58.