A ^{183}W, ^{1}H and ^{17}O Nuclear Magnetic Resonance Study of Aqueous Isopolytungstates

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Isopolytungstates have been studied in aqueous solution between pH 8 and 1.5, using ^{183}W, ^{17}O and ^{1}H NMR spectroscopy. The first polyanions to form upon acidification are the paratungstates A and B. Their resonances are largely assigned, and paratungstate B is shown to protonate with pK_a = 4.59. Its protonated form has at least two isomers separated by a detectably slow proton-exchange process. On further acidification, paratungstate B loses one tungsten atom to give an anion with no symmetry, which is identified as the solution form of ψ-metatungstate. This in turn protonates with pK_a = 2.65, before transmuting to the known species tungstate-Y. Six metatungstate species with Keggin structures are also observed at lower pH values. Five are metastable anions which slowly convert to the well known α-$[H_2W_{12}O_{40}]^{6-}$ ion. Two have β-Keggin structures. In each case direct structural information is provided from the solution state. The rotational correlation times and average interproton distances of the α- and β-$[H_2W_{12}O_{40}]^{6-}$ species are deduced from their ^{1}H NMR relaxation data, and similar data are used to assist in identifying the three internally monoprotonated α- and β-Keggin anions.

Although the aqueous chemistry of isopolytungstates is fundamental to the chemistry of both isopoly and heteropoly oxometalates,[1] progress in understanding it has been severely hampered by the slow attainment of equilibria and by the comparative inaccessibility of the NMR spectra of ^{183}W and ^{17}O in comparison with *e.g.* proton or vanadium. The species $[W_7O_{24}]^{6-}$ (paratungstate A),[2] $[H_2W_{12}O_{42}]^{10-}$ (paratungstate B),[3] $[H_2W_{12}O_{40}]^{6-}$ (α-Keggin, metatungstate),[2] $[H_4W_{11}O_{38}]^{6-}$ (an ion with σ_v symmetry, only known in the crystalline state)[4] and $[W_{10}O_{32}]^{4-}$ (tungstate-Y)[5] have been isolated from aqueous solution and fully characterised by X-ray crystallography. The metatungstate ion was in fact isolated as a triprotonated anion, but it is known to be only diprotonated in solution.[1] Paratungstates A and B interconvert in solution, as has been demonstrated by ^{17}O and ^{183}W NMR spectroscopy.[6] Their protonation has not been reported to date, apart from the tentative suggestion that an acid paratungstate, having approximately 16 protons per 12 notional $[WO_4]^{2-}$ units, forms as an intermediate in the preparation of tungstate-Y.[7] We show this to be a mixture of W_{12} and W_{11} species. Tungsten-183 NMR spectroscopy has also been used[8] to identify a β-Keggin isomer of $[H_2W_{12}O_{40}]^{6-}$ (tungstate-X), prepared by reduction and reoxidation of the α-Keggin species.[9] The same species has also been proposed as a transient intermediate.[1,4] The existence of a monoprotonated α-Keggin ion $[HW_{12}O_{40}]^{7-}$ has also been proposed,[7,8] again following an electrochemical preparation. In this case it was identified *via* the resonance of its trapped proton, together with polarographic data. It is described as reverting slowly to the diprotonated species in aqueous solution. However, neither of the above species has yet been structurally identified when the preparation only involves tungsten(VI). Two further and relatively transient isopolytungstate species have been described,[1,7] namely ψ- and ψ′-metatungstate. The ψ′ species, like $[HW_{12}O_{40}]^{7-}$ above, contains a trapped proton, and may in fact be the same species.[1] We show below that $[HW_{12}O_{40}]^{7-}$ indeed forms transiently in aqueous solution, without the involvement of redox processes. There is a good probability that ψ-metatungstate is the same as the solution precursor of $[H_4W_{11}O_{38}]^{6-}$ (above).[4]

An unsatisfactory feature of the above research is that it has largely depended on the isolation of compounds, rather than on the systematic investigation of solutions, over the available range of pH. We now describe such a solution study, using ^{183}W and, where possible, ^{17}O NMR spectroscopy. In respect of the paratungstates, it confirms the conclusions of Maksimovskaya and Burtseva,[6] whilst also revealing the protonation of paratungstate B and ruling out the simultaneous presence of any other major species. At lower pH values, paratungstate B is transformed into a hitherto unsuspected anion with 11 W atoms and no symmetry. In addition, six anions with either α- or β-Keggin structures can be identified. These vary in the sites and in the extent of their protonation.

Experimental

Spectra.—The ^{183}W, ^{1}H and ^{17}O NMR spectra were obtained on a Bruker WH400 spectrometer at 16.65, 400.13 and 54.2 MHz respectively. Tungsten-183 spectra were typically recorded using 2 mol dm^{-3} solutions at 20 °C with a 15 μs (30°) pulse length and 30 000 transients. The reference was capillary 2 mol dm^{-3} $Na_2[WO_4]$. The dependence of the ^{183}W shifts upon $[Li^+]$ was also recorded, by adding $LiCl{\cdot}H_2O$ (BDH) as appropriate. The tungsten shifts were also highly sensitive to temperature. Oxygen-17 spectra were obtained on the same solutions at both 20 and 99 °C with typically 20 000 transients, referenced to internal $H_2{}^{17}O$. They were repeated with altered offsets to identify spurious signals. The ^{1}H spectra were referenced to an aqueous sodium 3-(trimethylsilyl)propionate capillary. Measurements of T_1 were by the inversion-recovery method followed by least-squares fitting. Linewidths were measured by curve-fitting, and care was taken to minimise any contribution from pH drift.

Chemicals.—Stock tungstate solutions were prepared from WO_3 (BDH) and $LiOH{\cdot}H_2O$ (Aldrich) in *ca.* 50% $^{2}H_2O$, and adjusted to the chosen starting pH (see below) with dilute HCl, after filtration. Their volume was then reduced to requirements. Aliquots (3 cm^3) were then further acidified either directly or stepwise (see below). An M84 meter (Copenhagen) was used for measuring pH values, calibrated at room temperature using buffers of pH 4 and 7. Solutions were then left for at least 1 d, to approach equilibrium, and their pH was remeasured just after

Table 1 Tungsten chemical shifts and relative integrals of the more stable species

$[WO_4]^{2-}$	$[W_7O_{24}]^{6-}$	$[H_2W_{12}O_{42}]^{10-}$	$[H_3W_{12}O_{42}]^{9-}$
−9.5[a] (1 W)[b] [−2.4][c]	268 (1 W) [−0.42]	−109 (2 W) [−0.92]	−125 (2 W)
	−106 (4 W) [−2.1]	−114 (2 W) [−1.4]	−151 (2 W)
	−189 (2 W) [−1.8]	−116 (4 W) [−0.96]	−91 (4 W)
		−147 (4 W) [−1.8]	−140 (4 W)
$[H_7W_{11}O_{40}]^{7-}$	$[H_8W_{11}O_{40}]^{6-}$	α-$[HW_{12}O_{40}]^{7-}$	α-$[H_2W_{12}O_{40}]^{6-}$
−42 (*d*)	−36 (*d*)	−144	−123 [−0.83]
−104	−85		
−120	−114		
−120	−126		
−127	−118		
−137	−135		
−140	−148		
−164	−152		
−170	−166		
−178	−180		
−200	−209		
β-$[H_2W_{12}O_{40}]^{6-}$	$[W_{10}O_{32}]^{4-}$	$[W_{10}O_{32}]^{4-}$[e]	
−112 (3 W)	−105 (4 W)	−98 (4 W)	
−127 (6 W)	−118 (1 W)	−105 (1 W)	
−136 (3 W)			

[a] Tungsten chemical shift in ppm from external 2 mol dm^{-3} aqueous $Na_2[WO_4]$. [b] Relative tungsten integral. [c] Shift change per mol dm^{-3} Li^+ added. [d] All W_{11} resonances correspond to one W. [e] Tetrabutylammonium salt, in CD_3CN.

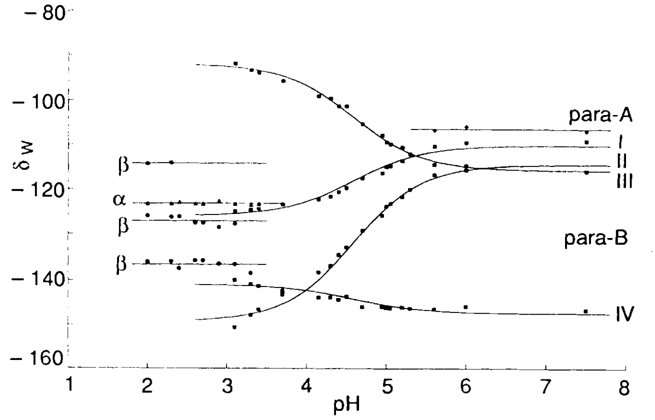


Fig. 1 Tungsten-183 chemical shifts *vs.* pH of species obtained by direct protonation of $[WO_4]^{2-}$ at 294 K

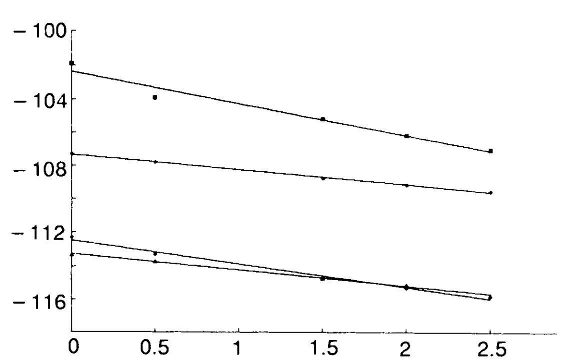


Fig. 2 Typical dependence of ^{183}W chemical shifts upon the concentration of added Li^+. Upper line, paratungstate A, 4 W resonance; and lower three lines, paratungstate B, resonances I, II and III

the spectra were obtained. Values of pK_a were obtained by linear regression analysis, using the simultaneous fitting of several shifts as far as possible. The very low sensitivity of tungsten NMR spectroscopy precluded any control of ionic strength. Solutions were generally 2 mol dm^{-3} in W. Oxygen-17 enrichment to *ca.* 5% was carried out by evaporation of a pH 6.5 solution followed by redissolution in $H_2{}^{17}O$ with added ^2H_2O. A similar evaporation method, using no isotopic enrichment initially, was used to prepare Keggin species with trapped protons, in ^2H_2O solution.

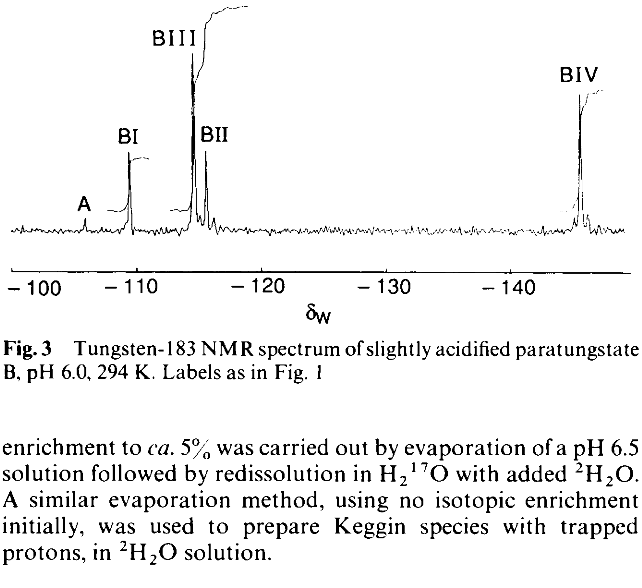


Fig. 3 Tungsten-183 NMR spectrum of slightly acidified paratungstate B, pH 6.0, 294 K. Labels as in Fig. 1

Results

Fig. 1 shows the tungsten chemical shifts observed at various pH values as aqueous $[WO_4]^{2-}$ is acidified. These shifts are found to depend quite strongly and linearly upon $[Li^+]$. The shift values for the component species, extrapolated where necessary, are reported in Table 1 along with their lithium dependence, where available, and their averaged integrals. Fig. 2 demonstrates the linearity of the $[Li^+]$ dependence. The resonances in Fig. 1 are labelled in accord with the discussion below. The proportions of paratungstate A (see below for assignment) are maximal at pH ≈ 6, at low concentration, low ionic strength and high temperature. A coupling of 18.5 Hz is observed for paratungstate B between tungstens II and IV. This is shown in Fig. 3. The relative heights of the resonances show that tungsten II couples to either of two tungstens IV, at the naturally abundant isotope ratio $^{183}W/^{184}W = 0.168:1$. The pH-dependent resonances in Fig. 1 all fit to a pK_a of 4.59 ± 0.03; the figure shows the fitted curves. Those of monotungstate and of paratungstate A are independent of pH.

Table 2 Linewidth variations for acidified paratungstate B

Peak label	^2H_2O, 283 K pH 2.8[a]	^1H_2O, 283 K pH 3.1	^1H_2O, 268 K pH 4.2[b]	^1H_2O, 268 K pH 3.1	$^1H/^2H$ pH ≈ 3
I	7.6[c]	3.4	3.0	6.0	2.8[d]
II	15.2	7.2	3.9	16.2	2.3
III	16.2	6.8	3.2	11.5	2.6
IV	5.2	3.0	2.3	4.6	2.8

[a] Almost fully protonated (*i.e.* H_3). [b] Just over half-protonated (*i.e.* $H_{2.6}$). [c] Width at half height in Hz, after removal of broadening due to window function. [d] After subtraction of natural linewidth = 1 Hz, as observed for the unacidified anion (*i.e.* H_2).

Table 3 Oxygen chemical shifts and relative integrals for paratungstates A and B

Peak label	A, $[W_7O_{24}]^{6-}$	B, $[H_2W_{12}O_{42}]^{12-}$	
a	74[a] (2 O)[b]	275 (4 O)	+4[c]
b	259 (2 O)	327 (2 O)	0
b′	319 (2 O)		
c	298 (4 O)	327 (4 O)	0
c′	648 (4 O)		
d	590 (2 O)	348 (4 O)	0
e	597 (2 O)	400 (4 O)	−3
f	648 (4 O)	424 (2 O)	*d*
g	626 (2 O)	465 (4 O)	−12
h		600 (4 O)	+4
i		605 (4 O)	+4
j		610 (4 O)	+6
k		646 (4 O)	+6
l		662 (2 O)	0

[a] Oxygen-17 chemical shift at 353 K, relative to solvent water. [b] Relative oxygen integral. [c] Shift upon partial protonation (see text). [d] Obscured at lower pH values.

The ^{183}W linewidths of paratungstate B increase with its extent of protonation. This increase in particularly marked at lower temperatures, and also when the solvent is predominantly ^2H_2O rather than ^1H_2O. The effect of deuteriation is to increase all the linewidths of paratungstate B by a factor of *ca.* 2.5. Some representative linewidths are listed in Table 2. The added linewidths correlate approximately but not exactly with the protonation shift of the resonance in question. Table 2 also reports that the excess linewidths approximately double, assuming a natural linewidth of 1 Hz, when the temperature is lowered by 15 K. This yields an enthalpy of activation of *ca.* 30 kJ mol⁻¹.

The ^{17}O resonances corresponding to the above species are listed in Table 3. Some of the integrals in this table are the combined contributions of overlapping peaks. It was convenient to separate the resonance sets for each species by the device of heating a pH 6 solution to 99 °C for 1 h, so as to maximise its proportion of paratungstate A, and then to cool it to room temperature before obtaining the oxygen spectrum. Appropriate subtraction of this spectrum from that of the equilibrium mixture at the same temperature yielded integrable spectra for each species separately. The half-life for return to equilibrium under these conditions was *ca.* 12 h. The oxygen NMR data for paratungstate B was insufficient for the reliable use of curve-fitting. However, the approximate shift changes between pH 7.0 (no added protons) and 4.5 (just over half protonated) are indicated in Table 3. The only oxygens to show a decrease in shift upon protonation of the anion are O_g and, to a lesser extent, O_e.

Below pH $\approx$ 5.5 the solutions are metastable. Upon prolonged heating they yield only the α-Keggin species (see below), and this is in any case the dominant species below pH 4. The tungsten resonances in Fig. 1, that are labelled β, belong to the more minor species that appears. The two at higher shift show the same mutual coupling of 19 Hz that was reported by Lefebvre *et al.*[8] The same solutions also show a proton resonance at δ 5.7, in addition to the expected α-Keggin proton resonance at δ 6.0.[10] The area ratio of these proton signals is the same as that of the corresponding tungsten resonances, within experimental error. This independently shows that the species labelled β-Keggin has two non-exchanging protons, as does the α isomer. The proton relaxation time measurements, described below, also confirm this.

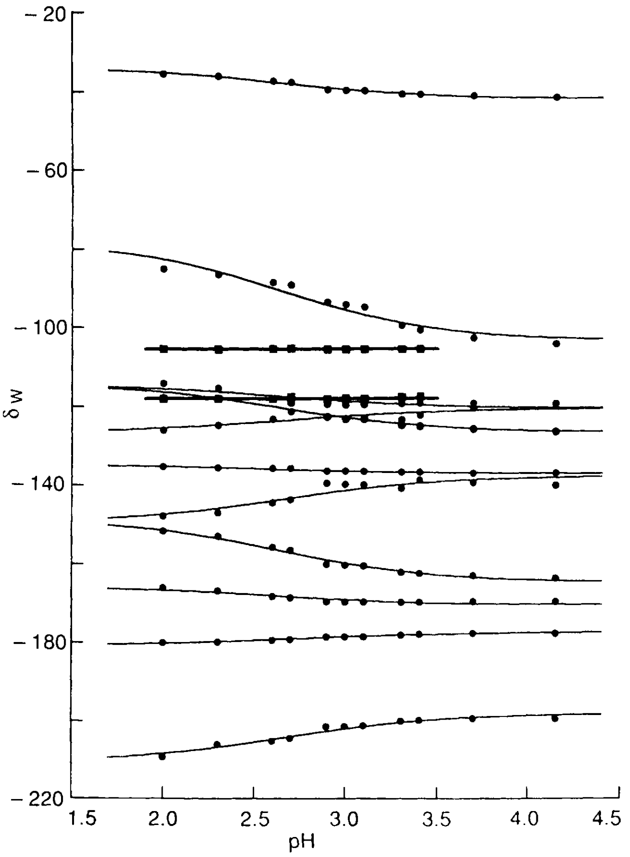


Fig. 4 Tungsten-183 chemical shifts *vs.* pH of two species that result from the metastability of protonated paratungstate B. ●, ψ-metatungstate; ■, tungstate-Y

Some rather different chemistry was observed upon carrying out a series of acidifications of a concentrated tungstate solution initially at pH 7.5. The dominant species in this initial solution was paratungstate B, along with a smaller amount of paratungstate A. At room temperature, acidification to pH values between 4 and 3 yielded 11 new tungsten resonances of equal area, in addition to the resonances from the α-Keggin and the protonated paratungstate B species, plus weak β-Keggin resonances (as above) between pH 3 and 4. The dependence of these new shifts upon pH is shown in Fig. 4, together with the fitted titration curves that yield a pK_a of 2.65 ± 0.04, and also two other pH-independent resonances that are observed only along with the 11-resonance species. Unfortunately, no couplings could be observed because the new 11-resonance species displays line broadenings at all pH values, similar to those observed with protonated paratungstate B. The line widths were somewhat variable, and no tungsten exchange was detected in a saturation-transfer experiment in which the broadest lines were pre-irradiated using a DANTE pulse sequence.[11] The new species showed essentially the same dependence upon metal concentration as the W_{12} species. It must therefore contain 11 tungsten atoms, rather than a multiple of this. Oxygen NMR spectroscopy was not attempted for this W_{11} anion because of its low concentration and high asymmetry. Further acidification gave the α-Keggin species.

Table 4 Oxygen-17 and ^1H chemical shifts and relative integrals for Keggin anions

α-$[HW_{12}O_{40}]^{7-}$	α-$[H_2W_{12}O_{40}]^{6-}$	β-$[HW_{12}O_{40}]^{7-}$	β-$[H_2W_{12}O_{40}]^{6-}$
127[a] (4 O)[b] [+][c]	80 (4 O) [+]	123 (1 O), 129 (3 O)	61 (3 O), 75 (1 O)[d]
411 (12 O) [−]	415 (12 O) [−]	*e*	397 (6 O), 402 (6 O)[e]
425 (12 O) [+]	418 (12 O) [+]	*e*	442 (3 O), 434 (6 O)[e]
700 (12 O) [+]	723 (12 O) [+]	765 (3 O)	725 (3 O), 764 (1 O)
5.8[f] (1 H)[g]	6.0 (2 H)	*h*	5.7 (2 H)

[a] Oxygen shift in ppm from solvent water, 294 K. [b] Relative oxygen integral. [c] Direction of shift change below pH 2. [d] Broad resonance. [e] Further resonances are present, but obscured by other peaks in this region. [f] Proton shift. [g] Relative proton integral per mole of anion. [h] Not resolved.

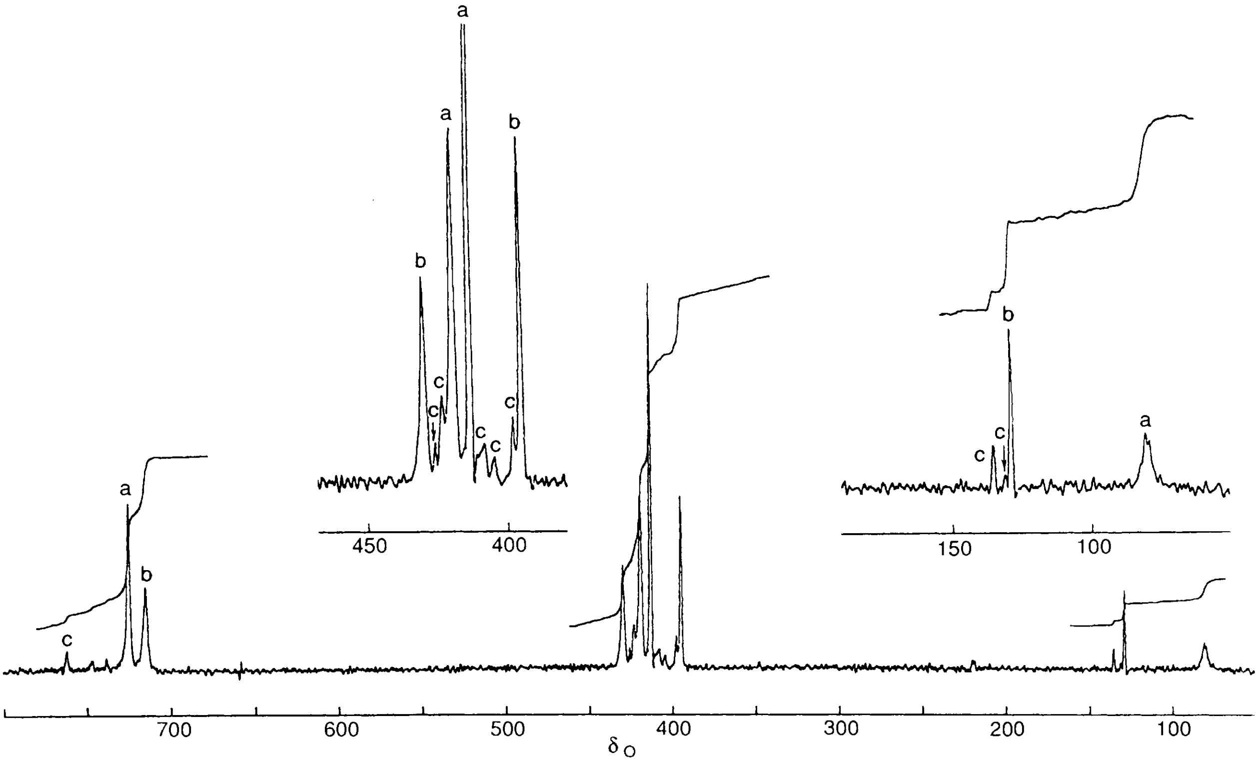


Fig. 5 Oxygen-17 spectrum at 353 K, pH 1.1, with inset expansions. Species: a, α-$[H_2W_{12}O_{40}]^{6-}$, metatungstate; b, α-$[HW_{12}O_{40}]^{7-}$, ψ'-metatungstate; c, probable β-$[HW_{12}O_{40}]^{7-}$. Each has undergone partial further protonation at this pH. The small unlabelled resonances only appear below pH 2.5

The two further and relatively weak resonances reported in Fig. 4 could be reliably discerned in the pH range 3.4–2.0. They were independent of pH, and favoured by low ionic strength. The peaks were in approximately 4:1 area ratio, and appeared at δ −105.2 and −118.0 respectively.

Different chemistry again was observed when the above pH 7.5 solution was acidified stepwise, with each step being followed immediately by a raising of the temperature to 99 °C. Under these conditions, also used to narrow the oxygen resonances, a single, new tungsten resonance appeared below pH 6.5, at δ −143.5. Its area was somewhat greater than that of the α-Keggin species at this pH value. It yielded a set of oxygen resonances (Table 4) rather similar to those from the α-Keggin, but still clearly resolvable from these. It also gave a resonance from an internal proton at δ_H 5.8, whose exchange with solvent D_2O was slow, the half-life being several days. Integration of this resonance alongside the α-Keggin resonance, in H_2O solution to prevent any loss of intensity, showed it to arise from a single trapped proton, and this conclusion was supported by an approximately twenty-fold increase in the proton's relaxation time (see below).

Further acidification, and also the passage of time, led to the progressive replacement of this internally monoprotonated species by the α-Keggin anion. However, its oxygen resonances could be traced down to pH 0.8. They showed some pH dependence below pH 2.5, as did the α-Keggin resonances, below pH 1.5, although the oxygens of lowest shift in both anions were not affected. The directions of these changes are indicated by signs in Table 4.

One further minor species was also detectable in the oxygen spectra only. Its proportion was about one third of the above monoprotonated species over the entire range of pH, and its resonances had rather similar shifts. As a result, not many were clearly resolved at pH > 2. However, spectra at pH < 2 showed that further oxygen resonances from this anion lie underneath those of its more abundant congeners. Two important shifts that are resolved are listed in Table 4. No separate proton resonance was resolved for this species. Fig. 5 shows a typical oxygen spectrum, in which all three resonance sets are visible.

Proton Relaxation Time Measurements.—The relaxation time T_1 was measured over a range of temperature for the three most stable internally protonated anions. The results are given in Table 5.

Table 5 Proton spin–lattice relaxation times *vs.* temperature for Keggin anions

T/K	α-$[HW_{12}O_{40}]^{7-}$	α-$[H_2W_{12}O_{40}]^{6-}$	β-$[H_2W_{12}O_{40}]^{6-}$
337		0.590 ± 0.001 *	0.462 ± 0.015
313		0.457 ± 0.009	0.404 ± 0.006
303		0.428 ± 0.008	0.392 ± 0.007
293	0.88 ± 0.02	0.418 ± 0.004	0.407 ± 0.005
283		0.426 ± 0.003	0.426 ± 0.004
263		0.573 ± 0.009	0.628 ± 0.002

* T_1/s.

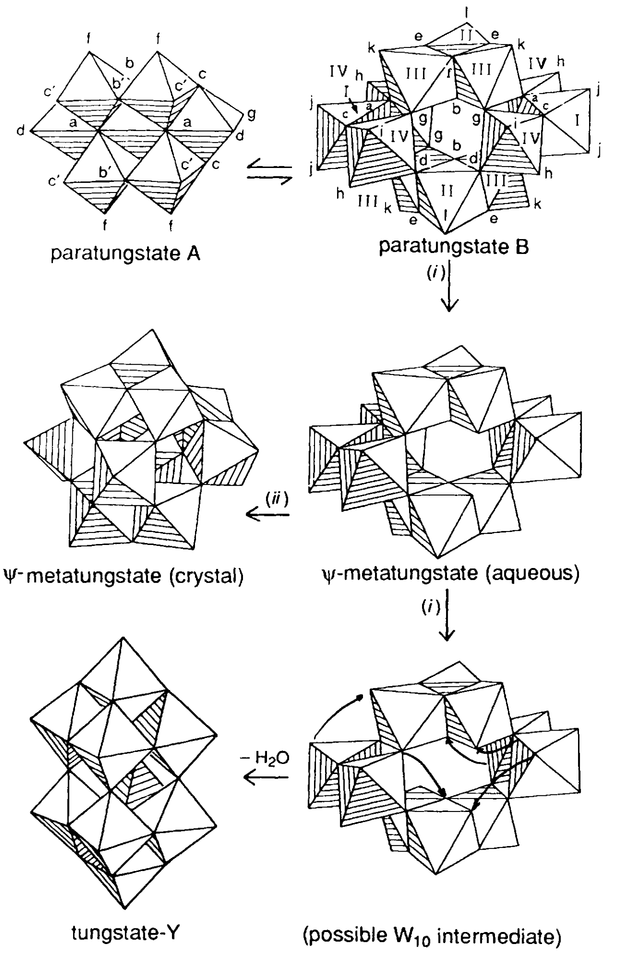


Fig. 6 Atom labels in paratungstates A and B, together with possible links with species that result from the acidification of B. (*i*) H^+; (*ii*) crystallisation

Discussion

Paratungstate Species.—The measurements above pH 6 essentially confirm the conclusions reached by Maximovskaya and Burtseva.[6] The increased field has, however, permitted more resolution, and the observation of one substantial W–W coupling. If one follows precedent in assigning this coupling to tungstens linked by a single oxygen,[8] then all the tungsten resonances of paratungstate B may be assigned as in Fig. 6. The corresponding resonances of paratungstate A (also in Fig. 6) are simply assigned by area. The oxygen assignments are more problematic, particularly for the less-symmetrical B species. The proposals in Table 3 depend on the inverse correlation of oxygen shifts with the length of the shortest M–O bond. This has considerable approximate support,[12,13] but is not reliable to high accuracy.

If we accept these assignments, at least provisionally, then the dominant protonation sites of paratungstate B must be at O_g, because only this resonance shows a substantial reduction in its shift, upon protonation;[14] O_e may be a secondary site of protonation. Polyanions generally protonate at their most highly substituted accessible oxygens, although this pattern may be slightly perturbed in subsequent protonations.[14] The most highly substituted oxygens in paratungstate B are O_a and O_b. These are both in the anion's central cavity. The O_a oxygens are probably inaccessible, and the two O_b oxygens are known to bind two protons in the crystal in any case.[15] This probably prevents their further protonation, along with that of some nearby oxygens, leaving O_g as the preferred site. Inspection of the structure of paratungstate B, in Fig. 6, shows that this site is internal, *i.e.* within the anion's cavity and not readily accessible to the solvent.

Although the dependence of the tungsten shifts of paratungstate B upon protonation is marked, it is not simply explained. The varying signs of the dependence are also unexpected. Theoretical considerations show that the chemical shift of a d^0 metal ion in a polyoxoanion framework can move in either direction when the framework is protonated, depending on the details of the changes in M–O bond lengths.[16] However, one finds for the decavanadate,[13,14] monomolybdononavanadate,[17] monotungstononavanadate[18] and the tetradecaphosphovanadate[13] anions that the vanadium shifts always decrease upon protonation. In these cases the protonation is necessarily at the exterior of the anion. The effect of interior protonation on a tungsten shift may be estimated from the data on the α-Keggin species in Table 1. It leads to an increase of 21 ppm. The change of sign probably arises because the metal atom now moves in a direction opposite to that for external protonation, within its oxygen framework. If we now regard the observed protonation at O_g as internal, then this explains the observed increases in shifts of tungstens III and IV upon protonation, for O_g bridges these tungstens. This argument also implies a concomitant deprotonation near to tungstens I and, especially, II. Tungsten II is nearest to the site of protonation of $[H_2W_{12}O_{42}]^{10-}$ in the crystal. Klemperer and co-workers[14] have already shown in the case of the decavanadate ion that its second and subsequent protonations cause a rearrangement of all the attached protons. A similar rearrangement probably occurs here.

However, the protonation of paratungstate B must be still more complex, because of the unexpected kinetic data implicit in Table 2. These clearly show that some motion involving protons is detectably slowed in the protonated (*i.e.* H_3) but not the unprotonated (H_2) anion. With some plausible assumptions regarding the shift separations and proportions of the exchanging species, one may deduce a deuteron residence time of the order of 10^{-4} s, using standard equations.[19] We suspect that one of the $[H_3W_{12}O_{42}]^{9-}$ isomers bears three internal protons, with two at O_g sites, and the other has one external proton, which moves rapidly between O_e sites. The exchange of a proton between the internal and the external sites would then be the rate-determining step.

It is not surprising to find that paratungstate A does not protonate, even though its molybdenum analogue (heptamolybdate) has a pK_a of 4.9. Polytungstates generally protonate less readily than their molybdenum analogues, and in any case the paratungstate resonances are not detectable below pH 5.5. We have not been able to observe the selective line broadening in the oxygen spectrum of A at high temperature, reported by Maximovskaya and Burtseva,[6] and clearly observed by both these authors and ourselves for heptamolybdate.[6,20] It is less surprising to find that monotungstate does not protonate within its range of observation (pH 14–5), because its reported pK_a is 3.5.[21]

The lithium dependence of the tungsten shifts of paratungstate A, given in Table 1, is much smaller for the central resonance, III, than for I or II, or for resonances II and IV of paratungstate B. The latter's I and III resonances have an intermediate dependence, which may reflect a reduced local affinity for Li^+, consonant with the absence of protonation in this region. Monotungstate has the steepest dependence of all, as expected for a sterically unhindered anion. All the lithium shifts are in the same direction as that expected for external protonation (see above). The Li^+ ion is too large to enter the cavities of either metatungstate or paratungstate B.

Maximovskaya and Burtseva also report that three of their oxygen resonances gain area in advance of the others upon addition of $H_2{}^{17}O$. There is some ambiguity about the assignment of these resonances, because of overlap. The possibilities are b, c, h, i and j. All but one of these candidate oxygens, using the above assignment, are attached solely to tungstens I and IV. These are the tungstens that each bear two terminal oxygens, and so their relative lability is not unexpected.

W_{11} *Species, ψ-Metatungstates.*—This species cannot be the $[H_4W_{11}O_{38}]^{6-}$ ion whose crystal structure has been reported by Lehmann and Fuchs,[4] even though it is prepared under similar conditions, because the ion observed here lacks symmetry. It is probable, however, that Lehmann and Fuchs' ion forms from the solution species by a process of oxygen elimination. We therefore give both species the identification put forward for the crystalline anion, *i.e.* ψ-metatungstate.

As the presence of protonated paratungstate B is essential for the appearance of the species with 11 equal tungsten resonances, one may reasonably assume that their structures are related. In any case, no fully unsymmetrical structure can be created by the simple removal of one WO_n unit from an α-Keggin anion. We propose a lacunary structure for the new species, based on the removal from paratungstate B of one W, of type IV, and its attached O atoms. This could yield a possible formulation $[H_7W_{11}O_{40}]^{7-}$ for the anion, along with the observed asymmetry.

All 11 tungsten resonances of this new species alter with pH, by comparable amounts. This precludes any simple identification of a protonation site. The similarity of the W_{11} resonances to those of paratungstate B includes selective line broadening, in both states of protonation, as well as protonation shifts in both directions. This implies that the W_{11} species bears protons in both of its states, and is similarly lacunary. This provides support for a formulation with several protons, some internal, and contrasts with the next species to be described.

Paratungstate B has been reported to yield tungstate-Y, $[W_{10}O_{32}]^{4-}$, upon further protonation, in the presence of large cations designed to disfavour Keggin structures.[5] This reaction involves low solubilities, and is therefore difficult to investigate in solution. However, our W_{11} anion could reasonably collapse with only modest rearrangement, to give the tungstate-Y structure, upon removal of a second similar WO_2 unit. Indeed, the narrow tungsten resonances reported above at δ −105.2 and −118.0, which appear under relatively acid conditions, have the correct area ratio to be the two tungsten resonances anticipated for tungstate-Y. A species with this relatively low charge would be favoured at lower ionic strengths, which is what we observe. We therefore make this tentative identification.

To corroborate this, we prepared the tetrabutylammonium salt of tungstate-Y by the method of Filowitz *et al.*[12] Its tungsten NMR spectrum showed two resonances in 4:1 area ratio at δ −98.0 and −104.8 respectively. These shifts are highly commensurate with the aqueous shifts above, after due allowance for the change of solvent and counter ion. The putative relationships between the above species are illustrated in Fig. 6.

Species with Keggin Structures.—The strong and relatively ubiquitous tungsten resonance at δ −123.0 must clearly arise from the α-Keggin anion $[H_2W_{12}O_{40}]^{6-}$. Its shift is equal to the δ −117.5 reported by the Na^+ salt by Lefebre *et al.*,[8] after re-referencing to allow for the altered experimental conditions. It also has the correct proton spectrum for an internally diprotonated species, and its oxygen spectrum shows four resonances in the anticipated area ratio 12:12:12:4, with appropriate shifts.

The three resonances which are labelled above as β-Keggin have the same relative areas, coupling and shifts relative to the α-Keggin resonance as do the β-Keggin resonances reported by Lefebvre *et al.*[8] The anion's proton resonance also has essentially the same shift as that reported by Launay *et al.*,[7] and the associated relaxation time is in the sub-second range expected for an internally diprotonated species. Thus we may be certain that β-$[H_2W_{12}O_{40}]^{6-}$ forms spontaneously in aqueous solution, as a minor species. Because it is only minor and transient we have not been able to identify all its oxygen resonances unambiguously. However, those we can identify (Table 4) are entirely consistent with a β-Keggin structure.

The main extra species that forms upon acidification of paratungstate, as distinct from acidification of monotungstate, gives an oxygen spectrum very similar to that of α-$[H_2W_{12}O_{40}]^{6-}$, with the same peak area ratio. It must therefore arise from an α-Keggin structure. One may discount the possibility of an ε-Keggin because its presence would almost certainly entail the simultaneous presence of γ- and δ-Keggin species, and these are not observed. The only marked differences of shift for the new α-Keggin species are the increase of 47 ppm for the central oxygens and the concomitant decrease of 23 ppm for the terminal oxygens. Both of these shifts are the expected consequence of the loss of an internal proton. They contrast with the shifts observed at much lower pH for both species. In these cases the internal oxygens are only very weakly affected, but one of the two bridging oxygens moves to markedly lower δ_O. These latter shifts are characteristic of external protonation.[14] Even stronger evidence that the new species is internally monoprotonated comes from its rather long proton relaxation time, some twenty times that of α-$[H_2W_{12}O_{40}]^{6-}$. It also forms preferentially at somewhat higher pH. We may therefore identify this anion as α-$[HW_{12}O_{40}]^{7-}$. In previous work this has only been made by reduction and reoxidation.[9] It reprotonates in solution with a half-life of *ca.* 1 d at room temperature and at pH *ca.* 5. Curiously, this reprotonation is not greatly speeded even at 99 °C.

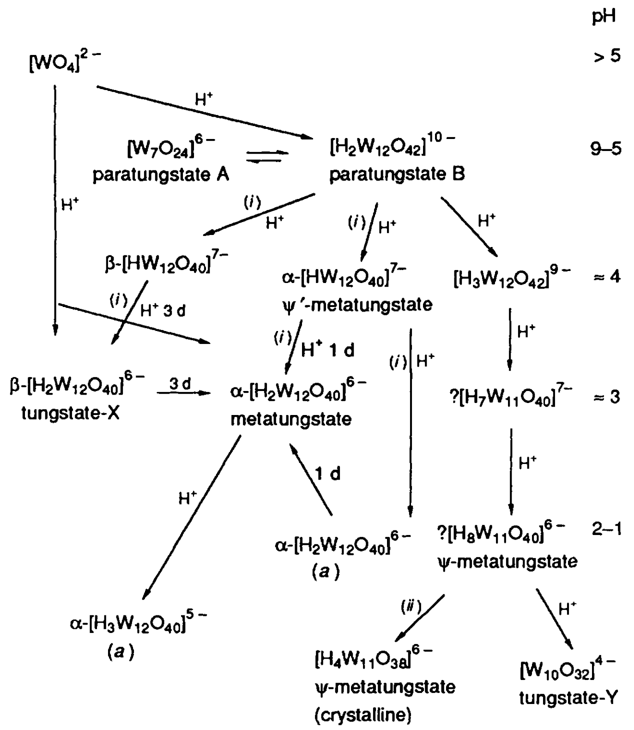
We find a proton shift of δ 5.8 for this species, which differs significantly from that of *ca.* 6.3 reported previously.[7] We also note that in D_2O solution the internal proton exchanges more slowly than that of the α-H_2 Keggin.

The more minor species whose intensity covaries with α-$[HW_{12}O_{40}]^{7-}$ is too dilute to yield a tungsten spectrum. However, its very similar oxygen shifts and its covariance are both highly consistent with a formulation β-$[HW_{12}O_{40}]^{7-}$. Thus we have evidence for non-electrochemical formation of both the internally monoprotonated and diprotonated Keggin species in both their α and β forms, and for the α forms also accepting external protons.

Relaxation Times.—It is convenient that the available temperature range spans the T_1 minima for both the α- and β-diprotonated Keggin species. This enables the reorientational correlation time τ_c for each species to be determined unambiguously over the range, by fitting the data using the formula (1).[19] The fitted relaxation rates were the differences

$$\frac{1}{T_1} = \frac{\mu_0{}^2\gamma_I{}^2\hbar^2 I(I+1)}{40\pi^2 r^6}\left(\frac{\tau_c}{1+\omega_I{}^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega_I{}^2\tau_c{}^2}\right) \qquad (1)$$

between those of the internally diprotonated species at various temperatures and the much smaller relaxation rate of the internally monoprotonated species at room temperature. The use of a difference in this way largely eliminates uncertainties about competing relaxation mechanisms. At 293 K, τ_c is 245 (α) and 314 ps (β). These are reasonable values for highly charged aqueous anions with this mass. The observed reorientation could in theory arise from a very rapid pseudo-rotation of the



Scheme 1 (*i*) Heat; (*ii*) crystallisation; (*a*) one proton is attached to the exterior of the anion

H–H vector driven by exchange between internal sites, but this seems far less probable than normal rotation. Any significantly slower internal motion would not contribute to τ_c. The slightly slower rotation of the β isomer is probably a consequence of its lower symmetry.

It requires slightly more assumptions to explain the actual values of T_1. If we assume that the difference in relaxation rates between the di- and mono-protio anions arises exclusively from the dipole–dipole interaction of the two internal protons, then we can also use equation (1) to calculate mean interproton distances of 1.89 (α) and 1.87 Å (β). These are slightly shorter than the 1.92 Å deduced from solid-state proton NMR spectroscopy of the α isomer.[20]

Conclusion

The present study shows the ability of solution-state NMR spectroscopy to elucidate the chemical relationships between species, and to detect new intermediates. Scheme 1 summarises these relationships.

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