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^{17}O NMR Determination of Proton Sites in Solid Heteropolyacid $H_3PW_{12}O_{40}$

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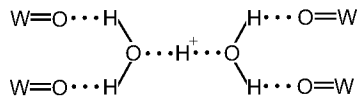
Comparison of chemical shift values for solid-state and solution ^{17}O NMR shows that, in the solid dehydrated $H_3PW_{12}O_{40}$, the terminal W=O oxygen atoms are the predominant protonation sites.

Keggin-type heteropolyacids (HPA), $H_{8-x}XM_{12}O_{40}$ [where X = Si^{4+}, P^{5+}, *etc.*; *x* is its oxidation state; M = Mo^{6+}, W^{6+}] are widely used as acid catalysts due to their strong Brönsted acidity together with their special anionic character.[1–3] Structural characterisation of the HPA proton sites is an important step towards understanding the catalytic activity. Bond length–bond strength correlations[4] as well as ^{17}O NMR data[5] indicate that in the free polyanions in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. In the free Keggin anion, edge-bridging M–O–M oxygens are assumed to be the predominant protonation sites.[4] $H_3PW_{12}O_{40}$, the strongest HPA in the Keggin series, is completely deprotonated in aqueous solution and partially deprotonated in polar organic solvents.[1] In solid HPAs, the protons take part in the formation of the HPA crystal structure, linking the neighbouring heteropolyanions (HPAN). In this case the more accessible terminal oxygens can be protonated.[6] Thus, from single-crystal X-ray and neutron diffraction data,[6] the proton sites in the crystalline $H_3PW_{12}O_{40}\cdot 6H_2O$ are represented as diaquahydrogen ions, $H_5O_2^+$, each of which links four neighbouring HPANs by forming hydrogen bonds with the terminal W=O oxygens (Scheme 1).

There are, however, no experimental data on the proton locations in dehydrated bulk HPAs, although such HPAs are widely used as catalysts.[1] Two options have been advanced. First, by analogy with HPA hydrates, protons in the



Scheme 1

dehydrated Keggin HPAs are assumed to be localized on the terminal M=O oxygens linking neighbouring HPANs in the crystal cell.[1] Alternatively, protonation of the bridging M–O–M oxygens has been suggested on the basis of IR band broadening upon dehydration of HPA.[7] However, IR studies have failed to unambiguously establish the protonation sites in polyanions. As demonstrated elsewhere, ^{17}O NMR is a sensitive probe for the determination of protonation sites in polyanions in solution.[5] We report here the ^{17}O MAS NMR determination of the protonation sites in dehydrated crystalline $H_3PW_{12}O_{40}$ (PW), which is the most important acid catalyst in the HPA series.[1]

All representative spectra are shown in Fig. 1. In the ^{17}O NMR spectrum of a 30 wt.% PW (0.12 mol dm^{-3}, pH 0) solution in D_2O [Fig. 1(*a*)] well-separated resonances for the terminal W=O (769 ppm from internal $D_2{}^{17}O$) and bridging W–O–W oxygens (two closely-spaced lines at 427 and 409 ppm for the edge- and corner-bridging W–O–W groups) are observed. This spectrum is fully consistent with those reported in the literature (chemical shifts in ppm from

external $H_2{}^{17}O$): 769, 431, 405 ($[Bu^n{}_4N]_3PW_{12}O_{40}$ in MeCN, 80 °C);[8] 767, 427, 408 ($PW_{12}O_{40}{}^{3-}$ in H_2O, pH 1, 25 °C).[4] Resonance of inner P–O–W oxygens is not seen due to lack of enrichment at this site.[8] Such agreement of all the solution spectra indicates the absence of protonation of the HPAN even in 30 wt.% PW aqueous solution.

We have observed, for the first time, ^{17}O MAS NMR spectra of ^{17}O-enriched solid PW [Fig. 1(*b,c*)].† As expected, these spectra contain a number of spinning sidebands and are more complex than the solution spectrum. Varying the spinning frequency in the range of 3.7–6.8 kHz has enabled us to determine the chemical shifts of all three centre bands present: 708 ± 5 (W=O), 440 ± 3, 400 ± 3 ppm (W–O–W) from external $H_2{}^{17}O$.‡ Clearly, there is good agreement between the solid-state and solution spectra.

But there are also distinct differences. First, the centre lines of the bridging oxygen resonance, which are close-spaced singlets in the solution spectrum, show partially resolved 300 to 600 Hz splittings in the solid-state spectrum, which is repeated in the spinning sidebands. As this splitting is not present in the solution spectrum, it must be attributed to a site symmetry in the crystal that is lower than the molecular symmetry, whereby chemically equivalent nuclei in the isolated molecule become magnetically inequivalent in the crystal lattice.[9] Second, the line of the terminal W=O oxygen in the solid-state spectrum is shifted 60 ppm upfield compared to the solution spectrum, whereas the bridging W–O–W oxygen resonances have the same chemical shifts within ±10 ppm in both spectra. This has important consequences as to the proton structure of solid PW.

As mentioned above, in aqueous solution the $PW_{12}O_{40}{}^{3-}$ anion is not protonated. In the solid PW, protons are localized on oxygen atoms in the HPAN upon dehydration of HPA.[1] When an oxygen site is protonated, the metal–oxygen bonds to that oxygen are weakened, leading to an upfield shift of its ^{17}O resonance.[5] Thus the terminal oxygens, since their resonance undergoes a pronounced upfield shift, are the predominant protonation sites. The large number of high intensity spinning sidebands for the signal centred at 708 ppm indicates an important chemical shift anisotropy for this type of oxygen, consistent with the protonation of this site. Therefore, ^{17}O MAS NMR unambiguously identifies the terminal W=O oxygen, rather than the bridging W–O–W oxygen, as the dominant protonation site in the dehydrated crystalline PW.

The proton structure given in Scheme 2 for the dehydrated PW is consistent with the data obtained and can be directly formed from that for PW hexahydrate (Scheme 1). Stoichiometrically, each proton is shared by four terminal oxygens like in PW hexahydrate,[6] since all the terminal oxygens in the PW crystal lattice are equivalent. We suggest that the

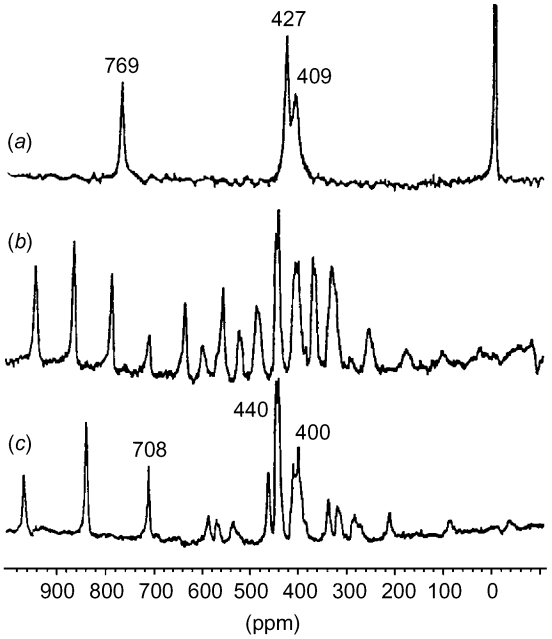
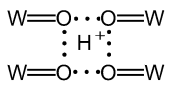


Fig. 1 ^{17}O NMR spectra of PW (3–5 atom% ^{17}O enrichment): (*a*) ^{17}O NMR spectrum of 0.12 mol dm^{-3} PW solution in D_2O, pH 0; (*b*) ^{17}O MAS NMR spectrum of solid PW pre-heated at 200 °C/0.4 mmHg for 2 h (4.2 kHz spin rate); (*c*) ^{17}O MAS NMR spectrum of solid PW pre-heated at 200 °C/0.4 mmHg for 2 h (6.8 kHz spin rate).



Scheme 2

proton migrates between four equivalent positions, W=O···H^+···O=W, and thus links four HPANs together, as the $H_5O_2{}^+$ ion does in Scheme 1. It should be noted that for this structure to be formed, the HPA cell volume should decrease upon dehydration, which is indeed the case.[10]

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† *Experimental.* 161.90 MHz ^{31}P and 54.24 MHz ^{17}O MAS NMR spectra were measured at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe. A few hundred (^{31}P) to several thousand (^{17}O) transient responses from 45°-(^{31}P)- or 20°-(^{17}O)-pulses, with repetition times of 2.0 s (^{31}P) and 0.1 s (^{17}O) were collected. Exponential multiplication with 5 Hz (^{31}P) and 50 Hz (^{17}O) line-broadening was applied prior to Fourier transformation. Special care was taken to protect solid samples from moisture.

3–5 atom% ^{17}O enriched PW crystalline hydrate was prepared from Na_2HPO_4 and ^{17}O enriched Na_2WO_4.[11] The latter compound was prepared by heating $Na_2WO_4{\cdot}2H_2O$ with water containing 10 atom% ^{17}O (from ICON, New Jersey, USA) in a sealed glass tube at 100 °C for 7 days.[12] The PW obtained, according to the ^{31}P MAS NMR (one single line, $\Delta\nu_{1/2}$ = 55 Hz, at –15.8 ppm from external 1% H_3PO_4 in D_2O, 4.4 kHz spin rate), contained >99 mol% Keggin HPA. Prior to ^{17}O MAS NMR measurements, the PW was heated at 200 °C/0.4 mmHg for 2 h to completely remove water from the sample.

‡ An estimate of the second-order quadrupolar shift showed that the positions of the centre bands will differ from the true isotropic chemical shifts by only a few ppm.