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In Situ FTIR Studies of the Protonic Sites of $H_3PW_{12}O_{40}$ and Its Acidic Cesium Salts $M_xH_{3-x}PW_{12}O_{40}$

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The dehydration mechanism of 12-tungstophosphoric acid $H_3PW_{12}O_{40}$ and of its acidic cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$, have been investigated by *in situ* FTIR spectroscopy at 240 K. Both protonic species and vibrational modes of the Keggin anions have been followed *in situ* as a function of the extent of dehydration. After being outgassed *in vacuo* at ambient temperature, di-aqua protons, $H_5O_2^+$, and/or hydroxonium ions, H_3O^+, species were detected for $H_3PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$ samples. These species are characterized by a $\delta(H_2O)$ vibration band at 1708 cm^{-1} and a $\nu(OH)$ vibration band at 3355 cm^{-1}. The intensity of these absorption bands progressively decreased as the protons were substituted by Cs^+. Further dehydration leads to the decomposition of the former protonic species with the formation of hydroxyl groups, characterized by a broad absorption band centered at ∼3209 cm^{-1}. After degassing at 673 K, the heteropolycompounds were completely dehydroxylated. The decomposition of protonic water clusters induced strong modifications of the vibration bands of the Keggin anion ascribed to changes in bond lengths and in the local symmetry of the anion. The extent of these modifications is closely connected to the proton content of the heteropolyacid. The $Cs_{2.7}H_{0.3}PW_{12}O_{40}$ sample showed only minor changes with dehydration. © 2001 Academic Press

Key Words: **polyoxometallates; 12-tungstophosphoric acid; Brønsted sites; hydroxonium ions;** *in situ* **infrared.**

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1. INTRODUCTION

Heteropolyoxometallates in their acid form, either as pure acids or as acid alkaline or transition metal salts, have been widely studied in relation to their catalytic properties for acid-type and mild oxidation reactions (1). In heterogeneous acid-type catalysis, heteropolyacid-based materials have been demonstrated to be very active in various reactions such as aromatic alkylation (2), isoparaffin/olefine alkylation (3), or alkane isomerisation (4). Often, heteropolyacids (HPAs) catalyse these transformations with higher efficiency than acidic zeolites, owing to their higher acid strenght. Most of the studies have been concerned with Keggin-type HPAs, particularly 12-tungstophosphoric acid, described as the strongest acid in the Keggin series.

For aromatic alkylation or *n*-butane isomerisation, the acid cesium salt of 12-tungstophosphoric acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, was shown by Misono and co-workers (2, 5) to be more efficient than its parent acid $H_3PW_{12}O_{40}$. Other groups have confirmed this finding. However, the Cs/P ratio value of the most active HPA, for *n*-butane isomerisation, was found to be close to 2 (4, 6). This was ascribed to their higher superficial proton content due to higher surface areas. Moreover, in addition to chemical composition, it is now well established that pretreatment conditions have a large influence on catalytic activity (5, 7) and selectivity (3). The concentration of protonic sites was correlated to catalytic activity (5, 7) while their nature was proposed to induce selectivity changes (3).

X-ray and neutron diffractions and also MAS-NMR techniques have been successfully applied to identify the structure of hydrated and/or partially dehydrated HPAs (8–10). From X-ray and neutron diffractions, the structure of the 12-tungstophosphoric acid hexahydrate was determined (8). The proton was shown to be coordinated to two water molecules in an $H_5O_2^+$ species (di-aqua proton) hydrogen bonded to four terminal $W{=}O_t$ oxide ions. The occupancy factor of the water O site was found to equal 0.5, confirming the formation of the di-aqua protons, $H_5O_2^+$, in the inter-Keggin anions space. Likewise, ^{17}O NMR allowed identification of different types of oxide ions of the Keggin anion (11), except for the PO_4 tetrahedron, which did not give rise to O exchange. The upfield NMR shift of the O_t resonance upon dehydration of polycrystalline $H_3PW_{12}O_{40}\cdot xH_2O$ was interpreted as an indication that protonation sites in the anhydrous form of $H_3PW_{12}O_{40}$ are the terminal oxide ions. However, based on IR spectroscopy data, the identification of protonation sites in anhydrous HPAs with Keggin structure gave rise to different interpretations. Both terminal oxygens ($M{=}O_t$) and/or bridged oxygens ($M{-}O{-}M$) were proposed (12, 13).

Additionally, IR and Raman spectroscopies have been used extensively to monitor the structural variations due

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to the nature of the heteroatom (X) and/or of the transition-metal element (M). Valuable information was obtained regarding the assignment of the absorption frequency of the $M{=}O$, $M{-}O{-}M$, and $X{-}O$ vibrations (14, 15). The sensitivity of these vibrations to structural changes and/or hydration state or partial replacement of protons by alkaline cations was also studied and frequency shifts were accounted for. The dehydration mechanism of 12-tungstophosphoric acid was investigated previously by Misono and co-workers (12). This study showed frequency shifts and splitting of the $\nu(W{=}O_t)$ and $\nu(W{-}O_c{-}W)$ vibrations of the Keggin anion with thermal treatment. From the comparison of IR spectra of $H_3PW_{12}O_{40}$ and $D_3PW_{12}O_{40}$ acids, the position of the proton in the anhydrous HPA was suggested to be the bridging oxygen $W{-}O_c{-}W$ rather than the terminal one. In a more recent paper, the same group compared the changes of the IR spectra of $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the 600- to 1300-cm^{-1} range. At 573 K, the same vibration frequencies were reported for both samples, and surprisingly, no significant modifications were observed up to 773 K desorption temperature, even for $H_3PW_{12}O_{40}$. It is worth noting that the previous two studies focused exclusively on analysing skeletal modes of the anion (absorption frequencies <1300 cm^{-1}), the absorption bands relative to the protonic sites $\nu(OH)$ and $\delta(H_2O)$ not being recorded. In another paper (16), the authors mentioned the presence of a broad band at 3224 cm^{-1} in the $\nu(OH)$ region and at 1712 cm^{-1} in the $\delta(H_2O)$ vibration range. Highfield and Moffat (17) also investigated the dehydration mechanism of 12-tungstophosphoric acid by photoacoustic FTIR spectroscopy in the 500- to 4000-cm^{-1} range. However, the spectra suffered from a large background and low resolution. Despite this drawback, the broad band centered at 3200 cm^{-1} and the peak at 1710 cm^{-1} were observed and assigned to the hydroxonium ion. After evacuation at 473 K, the latter band was reported to disappear, together with the appearance of new bands below 1300 cm^{-1}, ascribed to the distortion of the primary structure of the HPA. More recently, Southward *et al.* (18) presented an IR investigation of 12-tungstophosphoric acid and several of its salts (potassium, ammonium, and cesium). The specific absorption bands of Brønsted sites of HPA were not clearly identified and very similar absorption frequencies were observed for all samples.

In addition to the studies mentioned above, a description of the dehydration mechanism of 12-silicotungstic acid, by means of FTIR spectroscopy, was published recently by Bielanski *et al.* (19). The absorption bands observed at 3445 and 1700 cm^{-1} were assigned to $H_5O_2^+$ species.

As discussed above, up to now, the question of the nature of Brønsted acidity of 12-tungstophosphoric acid, and of its acidic cesium salts, has not been established unambiguously. We believe that IR spectrocopy studies partly failed to identify precisely the features of the protonic species of heteropolycompounds for three major reasons, namely, the strong absorption of the Keggin anion, the possible chemical reaction with catalyst holder, and the great sensitivity of the HPA toward rehydration. These technical difficulties and some artefacts such as partial rehydration may well have occurred and may explain discrepancies in the literature. From a catalytic point of view, the dependence of selectivity for acid-type reactions on the dehydration state of the HPA is an important feature (3). Therefore, it is essential to identify the nature of the protonic sites in a well-controlled hydration state. In a previous study, a close relationship was observed (20) between the vibration modes of the Keggin anion, $PW_{12}O_{40}^{3-}$, and the presence of the vibration bands ascribed to the protonic species, namely, the broad absorption in the vibration range of hydroxyl groups and that of the $\delta(H_2O)$ absorption near 1700 cm^{-1}, but the experiments were performed *ex situ* in classical IR cells. In the present investigation, our objective is to show the contribution of an *in situ* FTIR technique to the elucidation of structural changes of 12-tungstophosphoric acid and its cesium salts as well as the changes of their protonic species upon dehydration.

2. EXPERIMENTAL AND MATERIALS

The $H_3PW_{12}O_{40} \cdot 21H_2O$ sample was prepared according to a literature method (21) and purified through ether extraction and recrystallisation. The Keggin structure was confirmed by IR spectroscopy and ^{31}P MAS-NMR techniques. Its hydration level was determined by TGA using a Setaram 92-12 apparatus and its surface area was found to be equal to 7 m^2 g^{-1}.

Two Cs salts were prepared by adding stoichiometric amounts of an aqueous solution of cesium chloride (5 M) to the desired volume of 0.1 M aqueous solution of $H_3PW_{12}O_{40}$ as described in an earlier work (6, 7). The suspensions were stirred for 24 h at ambient temperature. Then, the precipitated salt was separated by centrifugation, washed twice with deionised water, and freeze dried. Two molar Cs/P ratios were chosen, 2 and 2.5. As expected, the two Cs salts have a cubic structure as shown by their XRD patterns and the anion corresponds to the Keggin structure as checked by IR spectrocopy (KBr pellet) and ^{31}PMAS-NMR. The chemical compositions were determined from chemical analysis of Cs and W contents. Hydration levels, after equilibrium under ambient atmosphere, were obtained by TGA. The two synthesised acidic Cs salts corresponded respectively to the $Cs_2HPW_{12}O_{40} \cdot 6H_2O$ and $Cs_{2.7}H_{0.3}PW_{12}O_{40} \cdot 10H_2O$ with BET surface area values equal to 61 and 134 m^2 g^{-1}, respectively.

For *in situ* FTIR studies, the HPA samples were dispersed in water and spread on an inert infrared transparent holder such as silicon or germanium (discs 1.5-mm thick and 17-mm diameter). The samples were placed in a specially designed IR cell, equipped with KBr windows, to allow IR measurements to be performed in temperature intervals between 113 and 723 K under the desired atmosphere. The IR cell was obviously carefully checked to be free of any leak. IR spectra were recorded on a Brucker IFS48 spectrometer and processed using the Vector software. For all experiments the recording temperature was chosen to be 240 K because it gave the better resolved spectra, enabling in particular clear detection of the shoulders.

3. RESULTS

All spectra were obtained by substracting the silicon or germanium background. Figure 1a shows the IR absorption spectrum of the $H_3PW_{12}O_{40}$ sample recorded under continuous vacuum at 240 K, following 30-min evacuation at increasing temperatures, in the 4000- to 400-cm^{-1} wavenumber range. The sample, subjected to evacuation at room temperature for 30 min, showed a strong absorption band centered at 3209 cm^{-1} with a prominent shoulder at 3355 cm^{-1} (see details in Fig. 1b) assigned to ν(OH) vibrations. In addition, an absorption band appeared at 1708 cm^{-1} assigned to $\delta(H_2O)$ vibration, as already reported by Misono and co-workers (16), Highfield and Moffat (17), Bielanski *et al.* (13, 19), and Essayem *et al.* (3, 20). TGA analysis, performed under the same conditions, showed that our HPA sample corresponded to $H_3PW_{12}O_{40} \cdot 5H_2O$, a state close to the stable hexahydrate form. The latter absorption, at 1708 cm^{-1}, is diagnostic of the presence of the protonated water clusters, probably the diaqua

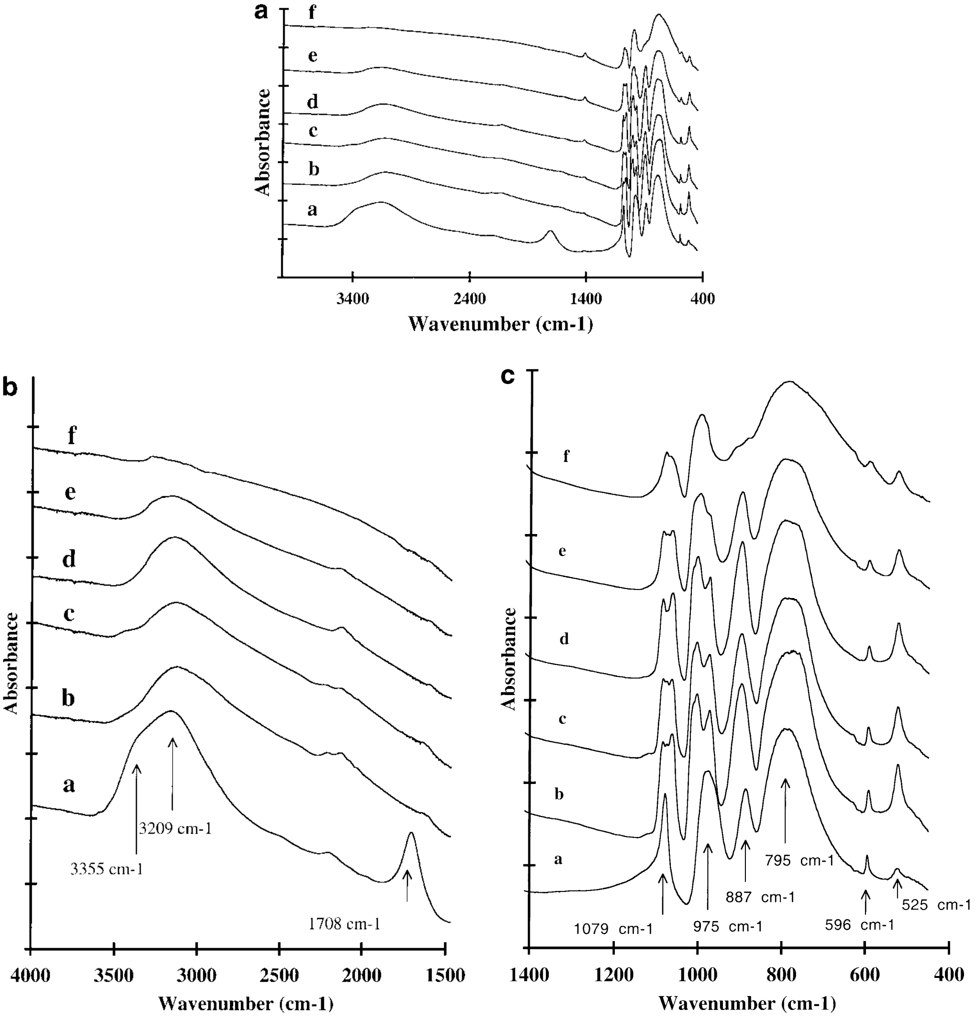
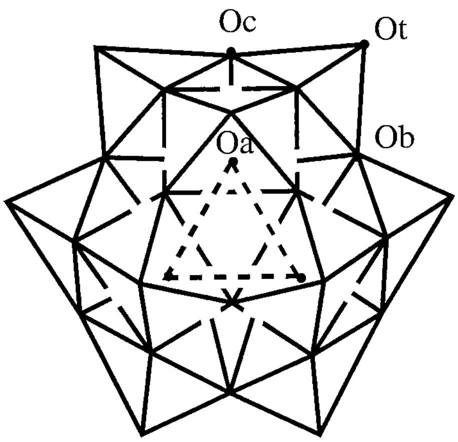


FIG. 1. (a) FTIR spectra of the $H_3PW_{12}O_{40}$ sample, recorded at 240 K, after thermal treatment under vacuum at different temperatures for 30 min. Wavenumber range: 4000–400 cm^{-1}. a, ambient temperature; b, 323 K; c, 373 K; d, 473 K; e, 573 K; f, 673 K. (b) FTIR spectra of the $H_3PW_{12}O_{40}$ sample, recorded at 240 K, after thermal treatment under vacuum at different temperatures for 30 min. Wavenumber range: 4000–1500 cm^{-1}. a, ambient temperature; b, 323 K; c, 373 K; d, 473 K; e, 573 K; f, 673 K. (c) FTIR spectra of $H_3PW_{12}O_{40}$, recorded at 240 K, after thermal treatment under vacuum at different temperatures for 30 min. Wavenumber range: 1400–400 cm^{-1}. a, ambient temperature; b, 323 K; c, 373 K; d, 473 K; e, 573 K; f, 673 K.



SCHEME 1. Oxygen sites in a Keggin unit.

proton $H_5O_2^+$, as shown to be present in $H_3PW_{12}O_{40} \cdot 6H_2O$ by X-ray and neutron diffractions studies (8), and/or hydroxonium ion, which has been recently identified by INS in partially dehydrated 12-tungstophosphoric acid (22, 23). The Keggin anion vibration bands appeared at 1079 cm^{-1} due to the $\nu_{as}(PO_a)$ vibration, 975 cm^{-1} due to the terminal $\nu_{as}(W{=}O_t)$ vibration, 887 and 795 cm^{-1} assigned to $\nu_{as}(W{-}O_b{-}W)$ and $\nu_{as}(W{-}O_c{-}W)$, respectively. Weaker absorptions appeared at 596 and 525 cm^{-1} due to $\delta(O{-}P{-}O)$ and $\nu_s(W{-}O{-}W)$, respectively (Fig. 1c).

The four distinct oxygen sites in a Keggin anion are represented in Scheme 1 and correspond to the following description:

—4 O_a belonging to the central tetrahedra PO_4;
—12 O_t, terminal oxygens linked to a lone tungsten atom;
—12 O_b in $W{-}O_b{-}W$ bridges, between two different W_3O_{13} groups;
—and 12 O_c, in a $W{-}O_c{-}W$ bridge, in the same W_3O_{13} groups.

Upon evacuation at 323 K, the $\nu(OH)$ band centered at 3209 cm^{-1}decreased in intensity while the shoulder at 3355 cm^{-1} disappeared altogether with the $\delta(H_2O)$ band at 1708 cm^{-1}. The $\nu_{as}(P{-}O_a)$ band was split into two bands at 1081 and 1065 cm^{-1}, the latter component being slightly more intense than the former one. Similarly, the $\nu_{as}(W{=}O_t)$ band was split into a triplet at 1014 cm^{-1} as a shoulder of the main central component at 1003 cm^{-1} and a distinct sharp component at 972 cm^{-1}. The $\nu_{as}(W{-}O_b{-}W)$ band initially at 887 shifted to 897 cm^{-1}. The broad feature at 795 cm^{-1}, ascribed to $\nu_{as}(W{-}O_c{-}W)$ or to an envelope of a number of such vibration bands, was not affected. Moreover, the $\nu_s(W{-}O{-}W)$ band increased in intensity and the $\delta(O{-}P{-}O)$ band was not affected.

As the evacuation temperature was increased, the broad $\nu(OH)$ band centered at 3209 cm^{-1} gradually shifted to a lower frequency: 3165 cm^{-1} at 373 K, 3145 cm^{-1} at 473 K, and several features could be distinguished at 573 K at 3275, 3217, and 3152 cm^{-1}, though the overall intensity decreased significantly. At 673 K, very weak bands were observed at 3697–3586, 3279, 3053, and 2914 cm^{-1} (Fig. 1b). Meanwhile, the low-frequency component of the $\nu_{as}(P{-}O_a)$ band at 1065 cm^{-1} decreased in intensity together with the low-frequency component of the band centered around 972 cm^{-1} while the band at 795 cm^{-1} broadened significantly (Fig. 1c). Similarly, the broad $\nu(OH)$ band was reduced dramatically and, eventually, disappeared upon evacuation at 673 K. At this temperature, the IR pattern, characteristic of the Keggin structure, was strongly modified and, in particular, the band at 887 cm^{-1} clearly disappeared. It is noteworthy that identical results were obtained using a Ge instead of a Si holder.

The IR spectra of the acid and its two Cs salts after evacuation at 298 K for 30 min are given in Fig. 2. A progressive decrease of the intensity of the $\nu(OH)$ vibrations at 3355 and 3209 cm^{-1} was observed with increasing Cs content together with the disappearance of the deformation band of the protonated water cluster at 1708 cm^{-1}. The optical density ratio of the $\delta(H_2O)$ band at 1708 cm^{-1} and $\nu(PO)$ band at 1079 cm^{-1} equals 0.302 and 0.102 for $H_3PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$, respectively. These values are in good agreement with proton content and suggest that the protonated water clusters in $H_3PW_{12}O_{40}$ and in $Cs_2HPW_{12}O_{40}$ are of the same size. For the $Cs_{2.7}H_{0.3}PW_{12}O_{40}$ sample the $\nu(OH)$ bands are hardly detected while the $\delta(H_2O)$ band is no longer present. Concerning the vibration of the Keggin anion, the four principal bands became narrower with the content of Cs^+ increasing.

The IR spectrum of $Cs_2HPW_{12}O_{40}$, evacuated for 30 min at 298 K (Fig. 2), was very similar to that of the acid. The main difference resides, firstly, in lower intensities of the $\nu(OH)$ bands at 3187 cm^{-1} and the shoulder at 3375 cm^{-1} and of the $\delta(H_2O)$ band at 1708 cm^{-1} and, secondly,

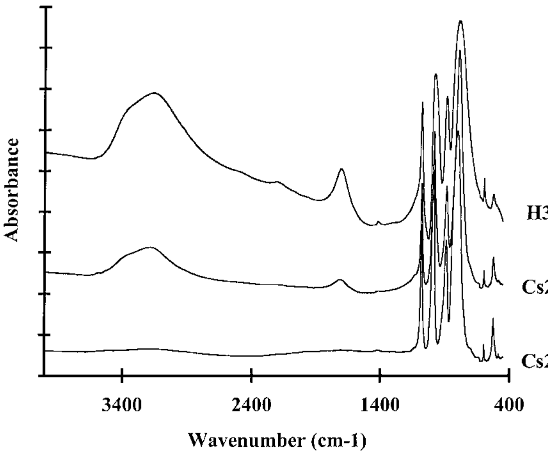


FIG. 2. FTIR spectra of $Cs_xH_{3-x}PW_{12}O_{40}$, recorded at 240 K, after evacuation at ambient temperature for 30 min.

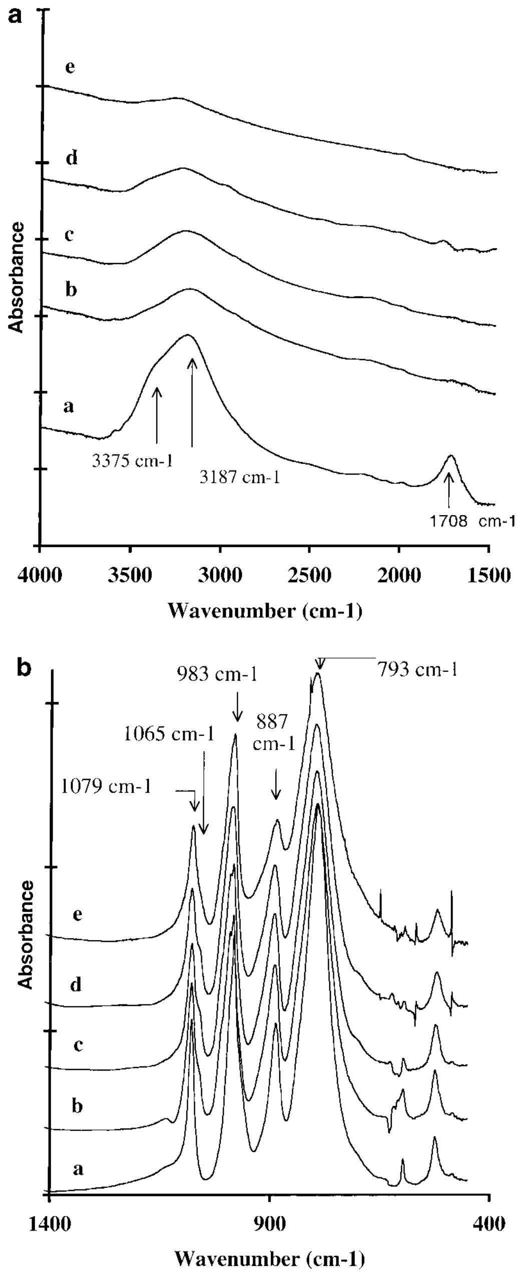


FIG. 3. (a) FTIR spectra of $Cs_2HPW_{12}O_{40}$, recorded at 240 K, after thermal treatment under vacuum at different temperatures for 30 min. Wavenumber range: 4000–1500 cm^{-1}. a, ambient temperature; b, 323 K; c, 373 K; d, 473 K; e, 573 K; f, 673 K. (b) FTIR spectra of $Cs_2HPW_{12}O_{40}$, recorded at 240 K, after thermal treatment under vacuum at different temperatures for 30 min. Wavenumber range: 1400–400 cm^{-1}. a, ambient temperature; b, 323 K; c, 373 K; d, 473 K; e, 573 K; f, 673 K.

narrower vibration bands of the Keggin anion. In addition, the $\nu_{as}(W{=}O_t)$ band presented a shoulder at 993 cm^{-1} in addition to the major peak at 983 cm^{-1} (Fig. 3b). Evacuation of $Cs_2HPW_{12}O_{40}$ at 323 K, which leads to the disappearance of the $\delta(H_2O)$ mode at 1708 cm^{-1}, revealed more differences: the $\nu_{as}(P{-}O_a)$ vibration was split into two components, with a main component at 1079 cm^{-1} and a minor shoulder at 1065 cm^{-1}. This is in contrast with the pure acid for which the low-frequency component was more intense (Fig. 1c). Likewise, the $\nu_{as}(W{=}O_t)$ vibration was also split into three components at 998–993–983 cm^{-1}. Few changes were observed for the $\nu_{as}(W{-}O_b{-}W)$ and $\nu_{as}(W{-}O_c{-}W)$ vibrations. Moreover, at variance with the pure acid, the $\nu_{as}(W{-}O_b{-}W)$ vibration was still detectable after evacuation at 673 K. Again, the progressive disappearance of the $\nu(OH)$ vibration at high temperature was observed simultaneously with the decrease in intensity of the shoulders at 998 and 1065 cm^{-1}.

The $Cs_{2.7}H_{0.3}PW_{12}O_{40}$ salt, evacuated at 298 K for 30 min, showed a similar pattern compared to that of the $Cs_2HPW_{12}O_{40}$ salt in the vibration range of the anion (Fig. 4). However, the $\nu(OH)$ band centered at 3200 cm^{-1} was very weak and no shoulder could be detected on either side of the absorption band (Fig. 2). Similarly, no absorption band at 1708 cm^{-1} was detected. More surprisingly, no absorption band was detected at 1640 cm^{-1} either, which would have shown the presence of neutral water. Moreover, the vibration bands of the Keggin anion appeared, once again better resolved than those of the $Cs_2HPW_{12}O_{40}$ sample (Fig. 2). In addition, while both the $\nu_{as}(P{-}O_a)$ and $\nu_{as}(W{=}O_t)$ bands are at almost the same frequency as those for $Cs_2HPW_{12}O_{40}$, the $\nu_{as}(W{-}O_b{-}W)$absorption appeared now as a major component at 890 cm^{-1} with a shoulder at 920 cm^{-1}. The $\nu_{as}(W{-}O_b{-}W)$ absorption maximum shifted

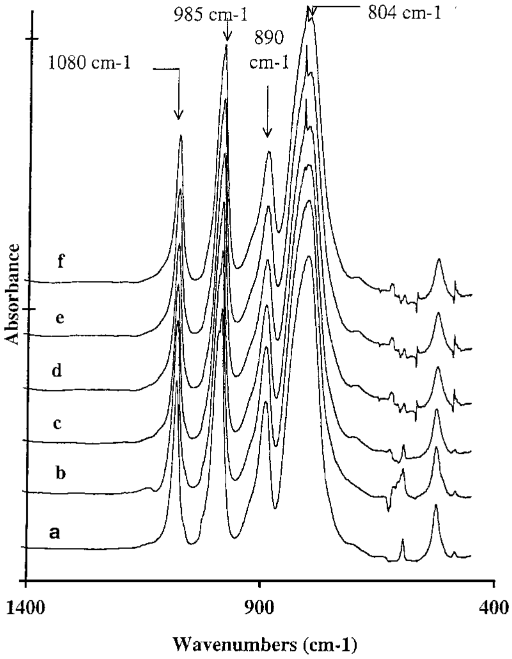
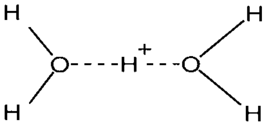


FIG. 4. FTIR spectra of $Cs_{2.7}H_{0.3}PW_{12}O_{40}$, recorded at 240 K, after thermal treatment under vacuum at different temperatures for 30 min. Wavenumber range: 1400–400 cm^{-1}. a, ambient temperature; b, 323 K; c, 373 K; d, 473 K; e, 573 K; f, 673 K.

to 804 cm^{-1} (Fig. 4). After evacuation at higher temperatures, the $\nu_{as}(W{=}O_t)$ and the $\nu_{as}(P{-}O_a)$ lines remained almost unchanged. Similarly, the $\nu_{as}(W{-}O_b{-}W)$ vibration was not modified at higher evacuation temperatures.

4. DISCUSSION

The presence of the $\nu(OH)$ shoulder at 3355 cm^{-1}, together with the $\delta(H_2O)$ vibration at 1708 cm^{-1}, and the parallel disappearance of both features as the evacuation temperature was increased or as H^+ ions were replaced for Cs^+ ions suggests that both absorptions are due to the same protonated water clusters, which were assigned by Brown *et al.* (8) to be the di-aqua proton, $H_5O_2^+$, in the 12-tungstophosphoric hexahydrate acid. The former spectroscopic features agree well with those described by Highfield and Moffat (17), Bielanski *et al.* (13, 19), and our previous results (20), but there only the $\delta(H_2O)$ feature at ~1710–1720 cm^{-1} was clearly noticed. However, it is still not clear whether the $\nu(OH)$ vibration associated with the $H^+(H_2O)_n$ should occur within the broad feature centered at 3200 cm^{-1}. This assignment is in agreement with the identification by Zecchina and co-workers (24, 25) in their investigation of the nature of the hydroxonium ion generated in strong acids such as H_2SO_4, CF_3SO_3H, HCl, and Nafion. They assigned the band in the 1750- to 1650-cm^{-1} range to the $\delta(OH\ldots O)$ *in-plane* deformation mode of the di-aqua proton, the peak in the 2700- to 3000-cm^{-1} range to its $\nu(OH)$ mode, and that at ca. 1200 cm^{-1} to its $\delta(OH\ldots O)$ *out-of-plane* deformation mode:



However, these absorptions should be broadened in view of the presence of additional ν, δ, and γ modes arising from solvation water.

As already mentioned above, TGA analysis showed that outgassing $H_3PW_{12}O_{40}$ at ambient temperature under vacuum for 30 min leads to the nearly 12-tungstophosphoric hexahydrate acid ($H_3PW_{12}O_{40} \cdot 5H_2O$). Therefore, we may assign the 1708-cm^{-1} band to the diaqua proton and/or hydroxonium ion $\delta(H_2O)$ mode and the shoulder at 3355 cm^{-1}, that disappeared simultaneously, to the $\nu(OH\ldots O)$ mode.

The IR spectra of the $Cs_{2.7}H_{0.3}PW_{12}O_{40}$ sample did not exhibit an absorption peak at 1708 cm^{-1} and did not show either a shoulder on the high-frequency side of the $\nu(OH)$ absorption in support of our assignment of this shoulder to $\nu(OH)$ vibration of the protonated water clusters. This assignment is also supported by the decrease of intensity of the shoulder as the cesium content increased.

As the $\nu_{as}(P{-}O_a)$ vibration occurring in all hydrated acid and salts (i.e., after vacuum, 30 min at 298 K) at the same frequency, it can be suggested that the Keggin unit is fully relaxed in the presence of either Cs^+ or $H_5O_2^+$, i.e. that these cations do not impose a strain strong enough to result in a significant alteration of the PO_4 tetrahedron.

Differences between the pure acid and its Cs salts appeared when considering the $\nu(W{=}O_t)$ band. Indeed, a general high-frequency shift was observed as the protons are substituted by Cs cations. This shift is probably due to the strengthening of the $W{=}O_t$ bond as the protonated water clusters are substituted by Cs cations. This arises probably from the strong hydrogen bonding between water molecules of the di-aqua proton and terminal oxide ions (O_t), resulting in a movement of the electron cloud from the tungsten toward the oxygen. Therefore, the $W{=}O_t$ bond is weakened, resulting in a lower frequency shift in presence of $H_5O_2^+$ by reference to Cs^+. The origin of the splitting of the $W{=}O_t$ absorption in the case of the salts into two components at 993–983 and 995–985 cm^{-1} for $Cs_2HPW_{12}O_{40}$ and $Cs_{2.7}H_{0.3}PW_{12}O_{40}$, respectively, is less clear. It may be suggested that the low-frequency component is associated with $W{=}O_t$ engaged in a hydrogen bonding with the residual $H^+(H_2O)_n$ species whereas the high-frequency component is associated with free $W{=}O_t$ only interacting with Cs^+ ions. The additional shift to high frequency as the cesium content is increased and the intensity increase of the high-frequency component under the same circumstances are in favour of this assignment.

As the temperature is increased and protonic water clusters are decomposed, the $\nu_{as}(P{-}O_a)$ band was surprisingly split into two components. In addition to the original band, an additional band appeared at 1065 cm^{-1}, whose intensity decreased as the proton content decreased (Fig. 3b). This additional band is more likely associated with the presence of acid sites. It may be suggested that the protons, liberated by the decomposition of the $H^+(H_2O)_n$ species, reacted with the most basic oxide ion (the terminal O_t), forming hydroxyl groups characterised by a $\nu(OH)$ vibration band at ~3300–3100 cm^{-1}. This interpretation is supported by the modification of the $\nu(W{=}O_t)$ mode upon dehydration while the other two skeletal modes $\nu(W{-}O_b{-}W)$ and $\nu(W{-}O_c{-}W)$ remained unchanged. The formation of such $W{-}O_t{-}H$ groups may induce asymmetry within the W_3O_{12} subgroups, thus modifying the bond energy of the central P–O bonds. Therefore, depending on whether or not Keggin units are interacting with protons, the original P–O frequency would be modified or not. The low-frequency shift is consistent with a weakening of the P–O bond as a result of a general withdrawal of electrons toward the incoming proton.

Previous ^{31}P NMR investigation of the $H_3PW_{12}O_{40} \cdot nH_2O$ has shown that, indeed, the ^{31}P NMR signal was sensitive to the hydration state. A lone resonance at −15 ppm was observed as long as the protonic water clusters were present, both for the acidic Cs salts and for the pure acid (23). Decomposition of the di-aqua proton (and/or hydroxonium ion) caused the ^{31}P signal to undergo an upfield shift and a broadening. Apparently, the NMR time scale did not allow, at the recording temperature, distinction between various ^{31}P screenings depending on the deformation of the Keggin ions that produced different $\nu_{as}(P{-}O)$ vibration frequencies. However, the broadening of the NMR signal indicates either an extended chemical shift domain or a dynamic oscillation of the Keggin structure, partially averaging out the chemical shift distribution. In addition, previous ^1H NMR studies also revealed a high mobility of the protons both before and after decomposition of the di-aquaprotons (23). Furthermore, Misono and co-workers clearly observed distinct ^{31}P NMR signals at 173 K that coalesced to a single peak at room temperature, indicating that protons from the di-aqua proton and eventually additional protons, hopping at room temperature, averaged out the magnetically nonequivalent phosphorous atoms (26).

The splitting of the $W{=}O_t$ vibration upon decomposition of the di-aqua proton into a number of components may arise from the same reason. The protons released when forming $W{-}O_t{-}H$ bonds result in a low-frequency shift of the $W{-}O_t$ vibration, owing to the lengthening of the $W{-}O_t{-}H$ bond. The remaining WO groups experience a symmetric contraction of the $W{=}O_t$ bond, which shifts the absorption to band higher frequencies. The absorption band at lower frequency is then expected to decrease in intensity as the number of protons decreases, and symmetrically, the high-frequency component intensity is also expected to decrease. This is actually observed by examining the changes of the $\nu(W{=}O_t)$ absorption that followed the disappearance of the $\delta(H_2O)$ absorption band as the protons are replaced by Cs.

The formation of $W{-}O_t{-}H$ bonds apparently causes significant asymmetry within the Keggin anions as observed by infrared spectroscopy, which suggests that on the infrared time scale the H atoms are static in contrast to those on the NMR time scale.

In addition, the asymmetry resulting from the decomposition of the di-aqua proton caused the $\nu_s(W{-}O{-}W)$ band to increase in intensity, presumably via an increase of the dipolar moment originating from the enhanced asymmetry of the subunit assembly.

As mentioned above, contrary to the case of the acid the almost neutral cesium salt $Cs_{2.7}H_{0.3}PW_{12}O_{40}$ exhibited the same single $W{=}O_t$ absorption, irrespective of the temperature of treatment. This indicates that Brønsted sites, when present, do not alter the symmetrical interaction of Cs cations with O_t ions, presumably because Cs ions are in an optimal, therefore stable, interaction in the inter-Keggin anion cavities.

Further dehydration of the pure acid causes much bigger disruption of the Keggin anion, as the peaks are much weaker in intensity and broader. In addition, no more OH groups could be detected at 673 K. This indicates that dehydroxylation has occurred, presumably by removal of oxygen ions from Keggin anions. The dehydroxylation could involve two terminal $W{-}O_t{-}H$ groups and reform a $W{=}O$ group and a coordinatively unsaturated tungsten ion. Such a scheme allows reversible rehydration as demonstrated elsewhere (12, 20).

The presence of a variety of OH groups generated by the decomposition of the protonated water clusters prior to total dehydroxylation is indeed an indication of the diversity of the proton location, at least from an energetic viewpoint. Even though, as seen from the perturbation of the $\nu_{as}(W{=}O_t)$ vibration mode, protons are mostly located at the terminal oxide ions. It may also be that, at higher temperature, a significant part of these protons could be located at other sites, including $W{-}O_c{-}W$ and even $W{-}O_b{-}W$ bridges. If such were the case, it is expected that the mobility of such protons would be quite different and that the generated OH would not be equally acidic.

5. CONCLUSION

From this *in situ* IR study, the following can be concluded:

1. The protonated species, which are present on 12-tungstophosphoric acid evacuated for 30 min at ambient temperature, are characterized by a discrete $\delta(H_2O)$ band at 1708 cm^{-1} and a broad $\nu(OH)$ band centered at 3209 cm^{-1} with a marked shoulder at 3355 cm^{-1}. These bands are ascribed to protonated water clusters $H^+(H_2O)_n$ with $n = 1$ or 2 (hydroxonium ion or di-aqua proton). As the outgassing temperature is increased, the $\delta(H_2O)$ peak at 1708 cm^{-1} and the shoulder at 3355 cm^{-1} are eliminated simultaneously, indicating that the protonated water clusters are decomposed. The formation of hydroxyl groups between the "liberated proton" and the terminal oxygen O_t of the Keggin anion is shown by the presence of a broad $\nu(OH)$ band at 3209 cm^{-1} and by modification of the vibration bands of the anion: a blue shift and a splitting of the $\nu_{as}(W{=}O_t)$ are observed, the extent of these modifications being linked to the H^+ content. Further evacuation is accompanied by a progressive decrease of the intensity of the $\nu(OH)$ absorption at 3209 cm^{-1}. At 673 K, complete dehydroxylation is obtained, producing the disappearance of the ν_{as} $(W{-}O_b{-}W)$ vibration peak.

2. The H^+ substitution with the Cs^+ ion to form $Cs_xH_{3-x}PW_{12}O_{40}$ agrees very well with the previous assignment; namely, a decrease of the intensity of the $\delta(H_2O)$ peak at 1708 cm^{-1} and of the $\nu(OH)$ vibration at 3209 and 3355 cm^{-1} (shoulder) is observed. Decomposition of the protonated water clusters is also observed when the temperature is increased, leading again to the formation of OH groups.

3. Narrower vibration bands due to the Keggin anion are observed as a result of the H^+ substitution by Cs^+. This is interpreted as due to a weaker interaction between Cs^+ ion and the Keggin anion, resulting in higher symmetry of the Keggin anion.

4. The variations of the IR spectra of $Cs_2HPW_{12}O_{40}$ and $Cs_{2.7}H_{0.7}PW_{12}O_{40}$ with outgassing are less pronounced than those observed with the pure acidic form. However, the dehydration mechanism is shown to be similar.

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