

Catalysis by Polyoxometalates

Part 3.—Influence of Vanadium(V) on the Thermal Stability of 12-Metallophosphoric Acids from *In Situ* Infrared Studies†

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The 12-molybdo(tungsto)phosphoric acids, and the related compounds 1-vanado-11-molybdo(tungsto)phosphoric acids, all having the Keggin structure, have been studied at different temperatures in a special infrared cell allowing experiments in a controlled atmosphere. The effects of dehydration and the thermal stability are discussed. The anhydrous acids are evidenced only for the two 12-molybdo- and 12-tungsto-phosphoric acids: for the vanado compounds, the results are in agreement with the release of vanadium from the host Keggin structure, when increasing the temperature and duration of the treatments in a dry atmosphere. The effect of exposure to water vapour after the thermal treatments is also discussed.

Heteropolyanions are now widely used as acid–base and/or redox catalysts in a great variety of chemical processes. Many important industrial reactions can be assisted by the use of these compounds, in a temperature range in which they are expected to be stable.¹

Among the heteropolyanions used, the 12-metallophosphoric acids related to the Keggin structure have attracted a special interest. The study of the different hydrates and of the thermal stability of the 12-molybdo- and 12-tungsto-phosphoric acids is not new (for *e.g.* the pioneering work in ref. 2), and has been undertaken by numerous teams. These compounds seem to be stable, respectively, up to 285 and 380 °C, when treated under dynamic heating.³ The introduction of vanadium in the structure leads to 1-vanado-11-molybdo- and 1-vanado-11-tungsto-phosphoric acids, which exhibit interesting catalytic properties,^{1b} the former being especially valuable in oxydehydrogenating reactions.⁴ Because of the industrial importance of these types of reaction, these compounds always attract the attention of many workers. A detailed study of their behaviour with respect to the temperature and the duration of the thermal treatments is of great interest in order to determine the nature of the active species responsible for the reactivity.

This paper deals then with an *in situ* IR study in a controlled atmosphere, at different thermal treatment temperatures, of four 12-metallophosphoric acids, namely $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and $\text{H}_4\text{PVW}_{11}\text{O}_{40}$, all crystallized with 13–14 H_2O . In the following, these compounds will be abbreviated, respectively, as PMo_{12}H , PW_{12}H , PMo_{11}VH and PVW_{11}H .

Experimental

Preparation of the Samples

The samples were prepared according to methods previously described: PMo_{12}H ,^{3a} PW_{12}H ,^{3a,5} PMo_{11}VH and PVW_{11}H .⁶ Purity was checked by polarography,^{3a,6b,7} ^{31}P NMR,^{6b,8,9} infrared spectrometry (IR),^{3a,6b} and thermogravimetry (TG).^{3a,6b} The number of water of crystallization molecules was obtained from the TG data.

Infrared Spectrometry

Spectrometer and Sampling

The IR spectra were recorded with a Perkin-Elmer 1700 FTIR spectrometer (spectral range down to 450 cm^{-1} , 10–20

scans, resolution 4 cm^{-1}). For the study of the thermal behaviour of the samples, finely ground compounds were deposited as a film as uniform as possible on a plate of NaCl, KBr or ZnSe, 2 cm in diameter. Then the plate was placed in the sample holder described below. In this way, the water molecules, and/or the other evolved products, could be freely evacuated during the heating process performed under vacuum or under gas flow. NaCl material transmits IR radiations down to 600 cm^{-1} , and KBr and/or ZnSe down to 400 cm^{-1} . NaCl and KBr are water sensitive and can react with the samples, NaCl being more inert than KBr. ZnSe is not water sensitive, and is expected to be the most inert of the three supports. However, it presents the disadvantage of sublimation at temperatures higher than 370 °C.

IR cell

The IR cell was designed to perform *in situ* experiments in a controlled atmosphere (vacuum, or gas flow at atmospheric pressure) with thermal treatments at temperatures up to 500–550 °C. The device consists of two Pyrex sections (noted A and B) clamped together *via* metal-to-glass seals and a Viton ring. The A section consists of a Pyrex tube provided with a gas inlet and outlet, and with connections to a conventional vacuum apparatus and a pressure gauge, fitted with grease-free taps. A chromel–alumel thermocouple enters the tube and is held at its axis using a Pyrex tube guide. The B section is equipped with KBr optical windows. The sample holder, made of Pyrex, consists of a guide tube welded to a piece with a circular hole on which the sample (powder deposited on a support plate) can be fitted and fixed.

In the vertical position, the entire device is located in the spectrometer, with the B section at the bottom. In that case, the sample holder is contained in the B lower part, and can be crossed by the IR beam. When the device is turned into the horizontal position, the sample holder can gently slide along the Pyrex tube and is then located just near the extremity of the thermocouple. It is then placed in an opening furnace and is submitted to thermal treatments at different temperatures for various durations. At the end of each heating, the sample is cooled down to room temperature (either under dynamic vacuum, or under gas flow). Then the taps are turned off, and the device is placed again in the vertical position allowing the sample holder to be in the B part, in order to record the IR spectrum.

The true sample temperature is difficult to evaluate, since the thermocouple is not located inside the sample. Although temperature gradients are likely to occur (Pyrex, NaCl, KBr

† Part 2: R. Thouvenot, M. Fournier and C. Rocchiccioli-Deltcheff, *J. Chem. Soc., Faraday Trans.*, 1991, 87, 2829.

and/or ZnSe are not good heat conductors), the sample temperature is approximated by the temperature given by the thermocouple located near the plate on which the powdered sample is deposited.

After each heat treatment followed by recording of the IR spectrum, either the sample holder is again returned to the furnace for another treatment or the taps are turned in, for checking the effect of the air humidity on the IR spectrum.

Results and Discussion

General Considerations

Several hydrates of the 12-metallophosphoric acids have been described and studied by X-ray diffraction methods. All the water molecules do not play the same role: some of them, implied in clusters such as H_3O^+ or H_5O_2^+ , are more tightly bound in the crystal structure. The highly hydrated compounds (29–30 H_2O) are not stable, and effloresce rapidly at room temperature, giving rise to hydrates with 13–14 H_2O , those of interest in this study (all these compounds are isotypic, see below).

The crystal structure of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{--}14 \text{ H}_2\text{O}$ was determined by d'Amour and Allmann^{10c} (triclinic, $a = 14.10 \text{ \AA}$, $b = 14.13 \text{ \AA}$, $c = 13.55 \text{ \AA}$, $\alpha = 112.1^\circ$, $\beta = 109.8^\circ$, $\gamma = 60.7^\circ$, $Z = 2$, $R = 0.079$). A triclinic 14-hydrate of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, isotypic with $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{--}14 \text{ H}_2\text{O}$, was evidenced by Fournier *et al.* ($a = 14.11 \text{ \AA}$, $b = 14.12 \text{ \AA}$, $c = 13.55 \text{ \AA}$, $\alpha = 112.04^\circ$, $\beta = 109.88^\circ$, $\gamma = 60.65^\circ$, $Z = 2$).¹¹ A stable 13-hydrate of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ is isotypic with $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{--}14 \text{ H}_2\text{O}$ (triclinic system, $a = 14.040 \text{ \AA}$, $b = 14.006 \text{ \AA}$, $c = 13.39 \text{ \AA}$, $\alpha = 112.10^\circ$, $\beta = 109.58^\circ$, $\gamma = 60.72^\circ$, $Z = 2$).¹¹ The behaviour of $\text{H}_4\text{PVW}_{11}\text{O}_{40}$ is similar: stable hydrate with 14 H_2O , triclinic symmetry ($a = 14.12 \text{ \AA}$, $b = 14.18 \text{ \AA}$, $c = 13.68 \text{ \AA}$, $\alpha = 112.06^\circ$, $\beta = 110.06^\circ$, $\gamma = 60.67^\circ$, $Z = 2$), isotypism with $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 14 \text{ H}_2\text{O}$.¹¹

Thermogravimetric analysis of the 13–14 hydrates shows a loss of weight as soon as the temperature is increased. Some modifications in the TG curves can be correlated with the existence of intermediary hydrates (8-hydrate for PMo_{12}H , PMo_{11}VH and PVW_{11}H , 6-hydrate for PW_{12}H). A plateau corresponding to the anhydrous acid is observed between 140 and 270 $^\circ\text{C}$ for PMo_{12}H , 200 and 360 $^\circ\text{C}$ for PW_{12}H , 150 and 270 $^\circ\text{C}$ for PMo_{11}VH , and 200 and 300 $^\circ\text{C}$ for PVW_{11}H (these temperatures correspond to heating under a dry nitrogen stream which is likely to influence the transformation kinetics: the temperature ranges are slightly different when heating without a gas stream³). With a further increase of the temperature, protons come off with oxygen from the polyanion, in the form of so-called 'constitution water' (1.5 H_2O for PMo_{12}H and PW_{12}H and 2 H_2O for PMo_{11}VH and PW_{11}VH). Above 450–500 $^\circ\text{C}$, only mixtures of oxides are characterized (typically by IR). The TG curves are consistent with previously published results.^{3,6b,11}

The two anions $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{PW}_{12}\text{O}_{40}^{3-}$ have the Keggin structure, which consists of one PO_4 tetrahedron surrounded by four M_3O_{13} groups ($\text{M} = \text{Mo}^{6+}$ or W^{6+}) formed by three edge-sharing octahedra. These trimetallic groups are linked together through oxygen atoms. A representation of this well known structure with coordination polyhedra is shown in Fig. 1, with the different types of oxygen atom (O_a , O_b , O_c , O_d). The IR spectra have been discussed and assigned previously;³ the most relevant features are as follows, depending on M (Mo or W) and on the number of water of crystallisation molecules: $\nu_{\text{as}}(\text{P}-\text{O}_a)$ (1080–1060 cm^{-1}), $\nu_{\text{as}}(\text{M}-\text{O}_d)$ (990–960 cm^{-1}), $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$ (900–870 cm^{-1}) and $\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$ (810–760 cm^{-1}). The $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$

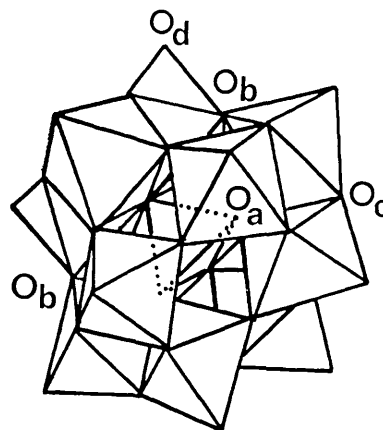


Fig. 1 Schematic polyhedral representation of the Keggin unit: O_a , oxygen atom common to the PO_4 tetrahedron and to a trimetallic group; O_b , oxygen atom connecting two trimetallic groups; O_c , oxygen atom connecting two MO_6 octahedra inside a trimetallic group; O_d , terminal oxygen atom

mode is particularly sensitive to the hydration degree, and undergoes a decrease of *ca.* 20 cm^{-1} through dehydration.^{3b,c} Vibrational spectra of 1-metallo-11-molybdo(tungsto)phosphates $\text{PM}'\text{M}_{11}\text{O}_{40}^{(9-n)-}$ related to the Keggin structure have already been reported and discussed as a function of the nature of the metal M'^{n+} ($n < 6$) introduced, considered as a perturbing element.^{3c,12} In these compounds, the typical pattern of the Keggin structure is modified as follows: the introduction of a metal M' other than Mo or W in the structure induces a decrease of the $\nu_{\text{as}}(\text{M}-\text{O}_d)$ stretching frequencies, and a possible splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band, depending on the nature of M' . The importance of this splitting, measured by the difference $\Delta\nu$ between the observed frequencies, can be considered as an indirect evaluation of the strength of the $\text{M}'-\text{O}_a$ interaction: the weaker $\Delta\nu$, the stronger the $\text{M}'-\text{O}_a$ interaction. The splittings are more important for the tungstic compounds than for the molybdic compounds, most likely because of the greater rigidity of the former. For the two compounds PMo_{11}VH and PVW_{11}H , in which one vanadium (V^{5+}) replaces one Mo or one W in the Keggin structure, the observed splittings (20 cm^{-1} for PMo_{11}VH , 24 cm^{-1} for PVW_{11}H , see Table 1) are relatively important, showing the weakness of the $\text{V}-\text{O}_a$ interaction. The other features of the IR spectra (see Table 1) agree with the general behaviour of substituted Keggin compounds.¹²

Previous work^{3a,13} has highlighted the different effects, acting as perturbations, that can be evidenced by vibrational spectrometry. The main effects are H bonding through the water molecules and/or the hydroxonium ions H_3O^+ or H_5O_2^+ , and electrostatic anion–anion interactions (X-ray diffraction data^{10,14} show that the anions are close to each other, even in highly hydrated compounds). The former effect induces a frequency decrease, the latter a frequency increase. In addition, from a vibrational study of the solutions of Keggin compounds in various solvents,¹³ it is found that the O_b atoms connecting two trimetallic groups (see Fig. 1) could be the most highly charged atoms of the polyanions. This can help to interpret the IR spectra obtained during the dehydration process through a discussion of the modifications of the frequencies of the Keggin unit induced by the above effects. (i) Dehydration progressively 'undresses' the hydrated protons and weakens the H bonding, the modes affected by the latter must therefore increase; (ii) a rearrangement of the packing is induced by the removal of water molecules, and this is clearly evidenced on three different hydrates of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, for

Table 1 Relevant frequencies (in cm^{-1}) and assignments of hydrated (13–14 H_2O) 12-metallophosphoric acids and related compounds containing vanadium

sample ^a	$\nu_{\text{as}}(\text{P}-\text{O}_a)$	$\nu_{\text{as}}(\text{M}-\text{O}_d)$	$\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$	$\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (13–14 H_2O)	1059 vs	979 sh 961 vs	895 m 880 sh	798 vs
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (13 H_2O)	1072 sh 1052 vs	980 sh 958 vs	885 m	790 vs
$\text{H}_3\text{PW}_{12}\text{O}_{40}$ (14 H_2O)	1077 vs	998 sh 979 vs	920 sh 905 m	808 vs
$\text{H}_4\text{PVW}_{11}\text{O}_{40}$ (14 H_2O)	1091 s 1067 vs	994 sh 972 vs	915 sh 897 m	799 vs

^a Powder on ZnSe plate, in air, prior to any treatment. vs = very strong; m = medium; sh = shoulder.

which interatomic distances between the next anions in the crystal lattice can be calculated from X-ray or neutron diffraction data,¹⁴ as shown in Table 2. For the 29-hydrate,^{14a,b} there are both short and long distances, and for the 6-hydrate,^{14d} the distances are almost equal and short enough to allow anion–anion interactions. The dehydration process induces both expansion and shrinkage of the room available between the anions, with a tendency for equalization of the distances between the closest neighbours in the network (isotropic distribution). An X-ray diffraction study performed at different temperatures¹¹ reveals the presence of a tetragonal form (not very far from cubic) which could be that of the anhydrous acid of PMo_{12}H and PW_{12}H : the anhydrous acids could consist of an almost isotropic distribution of protonated Keggin units in the framework. The protons would be localized on the most highly charged oxygen atoms, namely the O_b atoms: as a consequence, a decrease of the $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$ frequency would be expected. Some preferential interactions could occur, such as H bonding and electrostatic repulsion forces, consistent with the dimensions of the lattice cell (for PMo_{12}H , $a = 13.878 \text{ \AA}$, $c = 15.906 \text{ \AA}$, $Z = 4$; for PW_{12}H , $a = 13.75 \text{ \AA}$, $c = 15.96 \text{ \AA}$, $Z = 4$).¹¹

All the compounds studied exhibit IR spectra which depend on the sampling. Frequency shifts are observed, especially on the band usually assigned as $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$, depending on the nature of the plate on which the compound is deposited. KBr favours a partial dehydration of the starting material, which induces frequency shifts. NaCl is a more inert support, and can better approximate the true spectrum of the starting compounds (hydrates at 13–14 H_2O). ZnSe is expected to be still more inert than NaCl, and was preferred for our purpose to follow the thermal behaviour of the compounds in the IR cell described above. However, as ZnSe begins to sublime from 370°C , NaCl and KBr were also used for investigations at higher temperatures.

The first experiments were carried out under vacuum. As the thermal equilibria are slowly reached under vacuum, experiments under dry nitrogen or oxygen (flow rate *ca.* $80 \text{ cm}^3 \text{ min}^{-1}$) were performed, leading to similar results, but

more quickly. When using a nitrogen stream, a slight reduction of the sample was observed, but without significant changes with respect to the results obtained under oxygen. In order to avoid these reduction effects, all the experiments were therefore conducted under oxygen flow.

Thermal Behaviour of PMo_{12}H from an *In Situ* IR Study

Before any treatment, the IR spectrum of PMo_{12}H on a ZnSe plate exhibits the typical features of the Keggin structure, as shown in Table 1 and Fig. 2(1). Sweeping for 18 h under an O_2 stream at room temperature in the IR cell induces some modifications, especially on $\nu_{\text{as}}(\text{P}-\text{O}_a)$ and $\nu_{\text{as}}(\text{Mo}-\text{O}_d)$ [Fig. 2(2)]. The spectra obtained after a thermal treatment at 140°C do not depend on the duration [4 h or 18 h, Fig. 2(3) and (4)]: these spectra could be those of the anhydrous acid (see Table 3), likely to be the aforementioned tetragonal species observed by XRD.¹¹ The typical Keggin pattern is

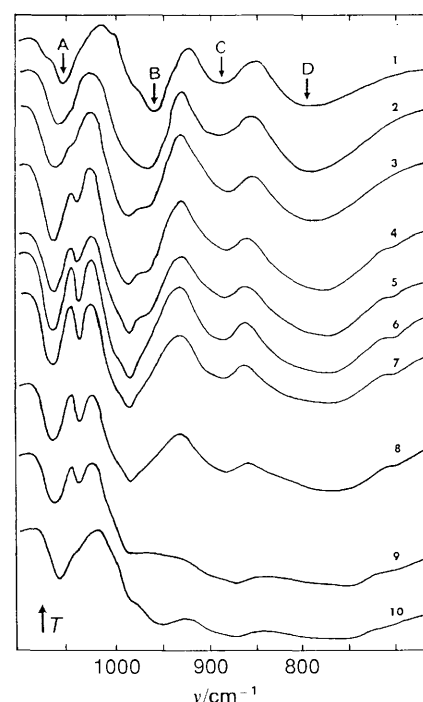


Fig. 2 IR spectra of PMo_{12}H (on a ZnSe plate) in the IR cell: all samples, except samples 1 and 7, are kept in a dry oxygen atmosphere (treatments under oxygen flow). 1, Initial sample in air, prior to any treatment; 2, 18 h at room temperature; 3, 4 h at 140°C ; 4, 18 h at 140°C ; 5, 20 h at 200°C ; 6, 18 h at 250°C ; 7, sample 6 after contact with the air humidity; 8, 18 h at 300°C ; 9, 36 h at 300°C ; 10, 68 h at 320°C ; 11, 18 h at 345°C ; 12, 18 h at 370°C . Bands: A, $\nu_{\text{as}}(\text{P}-\text{O}_a)$; B, $\nu_{\text{as}}(\text{M}-\text{O}_d)$; C, $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$; D, $\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$

Table 2 Interatomic distances (in \AA) between next anions in the crystal lattice of different hydrates of $\text{H}_3\text{PW}_{12}\text{O}_{40}$

$n\text{H}_2\text{O}$	$V/\text{\AA}^3$	Z	O_d-O_d	O_d-O_b	O_d-O_c	ref.
29	12604	8	3.614	4.559	2.806	14a, b
21	5136	4	2.992	3.387	2.966	14c
6	1794	2	3.344	3.407	3.213	14d

V = Cell volume; Z = number of formula units per cell; O_d-O_d , O_d-O_b and O_d-O_c = shortest distances between the O_d atoms of one anion and the O_d , O_b and O_c atoms of the next anions.

Table 3 Relevant frequencies (in cm^{-1}) and assignments of anhydrous 12-metallophosphoric acids

sample ^a	$\nu_{\text{as}}(\text{P}-\text{O}_a)$	$\nu_{\text{as}}(\text{M}-\text{O}_d)$	$\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$	$\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	1060 vs 1050 sh	989 vs 965 vs	877 m	795 vs
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	1079 vs	980 vs	923 sh 894 m	800 vs

^a Powder on a ZnSe plate, in the IR cell, after the thermal treatments explained in the text. vs = very strong; s = strong; m = medium; sh = shoulder.

preserved, with modifications with respect to the initial spectrum as follows: a broadening and slight splitting of $\nu_{\text{as}}(\text{P}-\text{O}_a)$ (shoulder at 1050 cm^{-1}), a significant increase of $\nu_{\text{as}}(\text{Mo}-\text{O}_d)$ with two marked absorption maxima, a strong decrease of $\nu_{\text{as}}(\text{Mo}-\text{O}_b-\text{Mo})$ (the slight decrease of $\nu_{\text{as}}(\text{Mo}-\text{O}_c-\text{Mo})$ is not very significant, because the broadness of this band increases, and the frequency is known to within $\pm 5\text{ cm}^{-1}$). According to the considerations developed above, these results can be explained as follows. (i) The O_d atoms were essentially implied in the H-bonding network with the H_3O^+ and H_5O_2^+ ions, since suppression of the network induces increase of the $\nu_{\text{as}}(\text{Mo}-\text{O}_d)$ frequency; the high values of the two frequencies of this composite mode are also consistent with the nearness of the Keggin units (both effects, nearness and suppression of H bonding, contribute to these high values). In the anhydrous acid, the O_d atoms are free from H bonding and close to those of the neighbouring anions; the presence of two $\nu_{\text{as}}(\text{Mo}-\text{O}_d)$ bands is consistent with the anisotropy of the packing. (ii) The important decrease of the $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$ frequency is in favour of the localization of the protons on the O_b atoms (likely to be the most highly charged, as explained above). (iii) The splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band is related to a weak distortion of the PO_4 tetrahedron induced by the anisotropy of its surroundings: we have mentioned above that preferential interactions could occur in the framework of the anhydrous acid, and the flexibility of the oxomolybdo framework can allow the transmission of the anisotropy and a broadening of the bridging vibrations.

On increasing the temperature, the anhydrous acid is always present [Fig. 2(5) and (6)], but significant broadenings are observed, especially at 250°C , showing that the sample can undergo a transformation. After the treatment at 250°C , the sample is exposed to air (and humidity): the resulting spectrum is very similar to the initial spectrum [compare Fig. 2(1) and (7), Table 1 and Table 4]. From 300°C , the IR spectrum shows that for the duration of the treatment the equilibrium is never reached [Fig. 2(8) and (9)]. After a treatment at 345°C for 18 h [Fig. 2(11)], irreversible collapse of the Keggin structure is evidenced (the typical pattern of the initial Keggin unit is not evidenced after exposing to water).

The treatment temperature was increased up to 370°C [Fig. 2(12)], showing a modification of the transformation products. At this temperature, ZnSe begins to sublime, as evidenced by the orange-pink deposit on the cold walls of the IR cell: this prevents further experiments at higher temperatures.

Because of the sublimation effect, we have performed similar experiments on a NaCl plate. The results are illustrated in Fig. 3. As with the ZnSe support, dehydration induces a decrease of the $\nu_{\text{as}}(\text{Mo}-\text{O}_b-\text{Mo})$ band (899 cm^{-1} for the starting material, 878 cm^{-1} after a treatment at 140°C for 20 h). The splitting of the $\nu_{\text{as}}(\text{Mo}-\text{O}_d)$ band is less pronounced than in the case of the ZnSe support, perhaps because water molecules could be partly trapped by the NaCl support. From 300°C , a mixture of species is observed. With treatments at 350°C and higher temperatures, the Keggin unit is destroyed, and mixtures of phosphates and molybdates are evidenced. The formation of sodium molybdate (band at 830 cm^{-1}) can be understood by considering that during the dehydration process, the water trapped on the NaCl support could react with it at a temperature higher than 350°C , giving rise to NaOH and HCl.¹⁵ The latter is evacuated with the gas stream, while the former reacts with the molybdenum oxide resulting from the destruction of the Keggin unit.

It appears that the thermal behaviour of PMo_{12}H is complicated by support effects at high temperatures. However, the experiments carried out allow the IR spectrum of the anhydrous acid to be obtained (see Table 3), and this differs from the spectrum of the hydrated acid essentially in the frequencies of the $\nu_{\text{as}}(\text{Mo}-\text{O}_d)$ and $\nu_{\text{as}}(\text{Mo}-\text{O}_b-\text{Mo})$ bands. It is also apparent that PMo_{12}H does not resist long treatments at temperatures higher than 300°C .

Thermal Behaviour of PW_{12}H from an *In Situ* IR Study

The IR spectrum of PW_{12}H on a ZnSe plate before any treatment is shown in Fig. 4(1) and the frequencies are listed in Table 1. After 17 h sweeping of the sample under an O_2 stream at room temperature in the IR cell, the spectrum undergoes some modifications, essentially on the

Table 4 Relevant frequencies (in cm^{-1}) and assignments of 12-metallophosphoric acids and related compounds containing vanadium after heating followed by water exposure

sample ^a (heating, water exposure)	$\nu_{\text{as}}(\text{P}-\text{O}_a)$	$\nu_{\text{as}}(\text{M}-\text{O}_d)$	$\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$	$\nu_{\text{as}}(\text{O}_c-\text{M})$
PMo_{12}H	1060 vs	980 sh	887 m	800 vs
250°C , 18 h		963 vs		
PMo_{11}VH	1057 vs	980 sh	882 m	790 vs
190°C , 15 h		960 vs		
PW_{12}H	1077 vs	998 sh	920 sh	808 vs
320°C , 21 h		979 vs	907 m	
PVW_{11}H	1078 vs	980 vs	900 m	808 vs
340°C , 18 h				

^a Powder on a ZnSe plate, heating under oxygen flow in the IR cell, followed by water exposure. vs = very strong; m = medium; sh = shoulder.

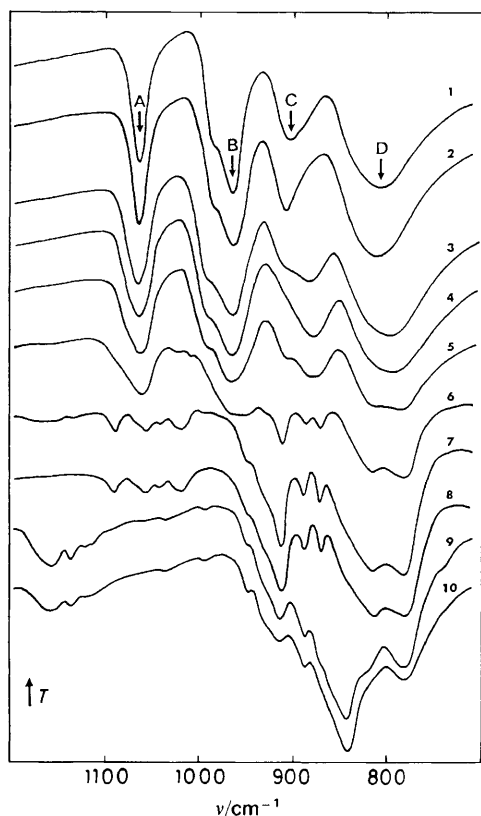


Fig. 3 IR spectra of PMo_{12}H (on an NaCl plate) in the IR cell: all samples, except samples 1 and 8 are kept in a dry oxygen atmosphere (treatments under oxygen flow). 1, Initial sample in air, prior to any treatment; 2, 17 h at room temperature; 3, 18 h at 140°C ; 4, 70 h at 200°C ; 5, 18 h at 250°C ; 6, 18 h at 300°C ; 7, 18 h at 350°C ; 8, sample 7 after contact with the air humidity; 9, 72 h at 370°C ; 10, 18 h at 400°C . Bands: A, $\nu_{\text{as}}(\text{P}-\text{O}_\text{a})$; B, $\nu_{\text{as}}(\text{M}-\text{O}_\text{d})$; C, $\nu_{\text{as}}(\text{M}-\text{O}_\text{b}-\text{M})$; D, $\nu_{\text{as}}(\text{M}-\text{O}_\text{c}-\text{M})$

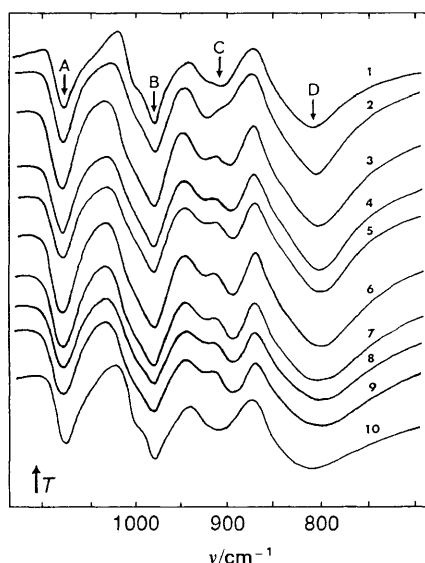


Fig. 4 IR spectra of PW_{12}H (on a ZnSe plate) in the IR cell: all samples, except samples 1 and 10, are kept in a dry oxygen atmosphere (treatments under oxygen flow). 1, Initial sample in air, prior to any treatment; 2, 17 h at room temperature; 3, 68 h at 80°C ; 4, 18 h at 150°C ; 5, 18 h at 200°C ; 6, 18 h at 250°C ; 7, 18 h at 300°C ; 8, 70 h at 300°C ; 9, 21 h at 320°C ; 10, sample 9 after exposure to air humidity. Bands: A, $\nu_{\text{as}}(\text{P}-\text{O}_\text{a})$; B, $\nu_{\text{as}}(\text{M}-\text{O}_\text{d})$; C, $\nu_{\text{as}}(\text{M}-\text{O}_\text{b}-\text{M})$; D, $\nu_{\text{as}}(\text{M}-\text{O}_\text{c}-\text{M})$

$\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ band [Fig. 4(2)]. A thermal treatment under O_2 flow at 80°C for 68 h modifies the shape of this band (two separated maxima at 923 and 897 cm^{-1}). The spectra displayed in Fig. 4(3)–(9) are practically independent of the treatment temperature (150 – 320°C) and of the duration [see, for instance, Fig. 4(7) and (8) relative to a treatment at 300°C , respectively, for 18 h and 70 h]. We can thus consider that an equilibrium is reached, and that all these spectra are characteristic of the anhydrous acid (see Table 3). As in the case of PMo_{12}H , the Keggin pattern is preserved, but the modifications with respect to the initial spectrum are not so pronounced. The most striking feature is the modification of the $\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ band: the frequency decrease of its low-frequency component is consistent with the localization of protons on the O_b atoms, as for PMo_{12}H . The high-frequency component of the $\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ band, at 923 cm^{-1} , could be due to motions involving non-protonated O_b atoms (the rigidity of the oxotungsto framework would allow discrimination between both protonated and non-protonated O_b atoms, when only a mean effect is observed for PMo_{12}H , the oxomolybdo framework being less rigid). Since the H_5O_2^+ are initially connected to the O_d atoms through an H-bond network, as evidenced by neutron diffraction,^{14d} the suppression of the H bonds during the dehydration process ought to induce an increase of the $\nu_{\text{as}}(\text{W}-\text{O}_\text{d})$ frequency. Since it remains unchanged (the $\nu_{\text{as}}(\text{W}-\text{O}_\text{d})$ band essentially undergoes broadening, without any frequency shift), we could suggest that the Keggin units in the anhydrous form are further from each other than in the 6-hydrate (a decreasing effect which may counterbalance the increasing effect induced by the suppression of the H bonds). The $\nu_{\text{as}}(\text{P}-\text{O}_\text{a})$ band only undergoes broadening, without any splitting: the rigidity of the oxotungsto framework probably does not favour a second-order effect on the symmetry of the encaged tetrahedron. After the treatment at 320°C [Fig. 4(9)], the sample is exposed to the air humidity: the initial spectrum is obtained again, showing that the starting hydrate is restored (see Table 4, cf. Table 1). Taking into account the sublimation tendency of ZnSe , further experiments at higher temperatures have not been carried out.

Experiments performed on a KBr plate give similar results, as long as the treatment temperature is not too high. After a treatment at 350°C for 18 h, a mixture of PW_{12}H and other species, probably phosphates and polytungstates, is clearly evidenced. On increasing the treatment temperature, the Keggin structure is completely destroyed. By comparison with the results obtained with PMo_{12}H on an NaCl plate, we can conclude that KBr could react at high temperature with water vapour and the WO_3 resulting from the decomposition of PW_{12}H , giving rise to complex mixtures of polytungstates.

Thermal Behaviour of PMo_{11}VH from an *In Situ* IR Study

The results obtained with PMo_{11}VH deposited on a ZnSe plate are shown in Fig. 5. Before any treatment [Fig. 5(1), Table 1], the IR spectrum is very similar to that of PMo_{12}H : as mentioned above, the introduction of V in the Keggin structure induces a slight decrease of the $\nu_{\text{as}}(\text{M}-\text{O}_\text{d})$ frequency and a splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_\text{a})$ band, observed at 1052 cm^{-1} with a shoulder at 1072 cm^{-1} (lowering of the symmetry of the PO_4 tetrahedron, see ref. 12). A sweeping under O_2 flow at room temperature, and different heatings for variable durations [Fig. 5(2)–(7)], modify the pattern in the region of the $\nu_{\text{as}}(\text{P}-\text{O}_\text{a})$ band: disappearance of the 1072 cm^{-1} shoulder, progressive growth of a band at 1037 cm^{-1} , shift of the most intense maximum towards higher frequencies (up to 1064 cm^{-1}). Similarly the $\nu_{\text{as}}(\text{M}-\text{O}_\text{d})$ band,

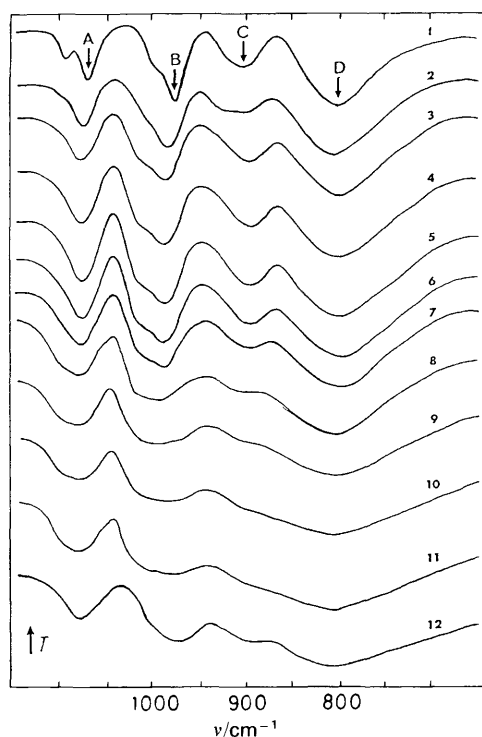


Fig. 5 IR spectra of PMo_{11}VH (on a ZnSe plate) in the IR cell: all samples, except samples 1 and 10, are kept in a dry oxygen atmosphere (treatments under oxygen flow). 1, Initial sample in air, prior to any treatment; 2, 4 h at room temperature; 3, 15 h at 190°C ; 4, 116 h at 190°C ; 5, 17 h at 240°C ; 6, 17 h at 275°C ; 7, 20 h at 300°C ; 8, 20 h at 325°C ; 9, 90 h at 325°C ; 10, sample 9 after exposure to air humidity. Bands: A, $\nu_{\text{as}}(\text{P}-\text{O}_a)$; B, $\nu_{\text{as}}(\text{M}-\text{O}_d)$; C, $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$; D, $\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$

which includes motions of $\text{Mo}-\text{O}_d$ and $\text{V}-\text{O}_d$ vibrators, undergoes modifications with the temperature and duration of the thermal treatments: broadening of the unsymmetrical starting band, splitting into two bands at 985 and 965 cm^{-1} (similar to the bands observed in the spectrum of anhydrous PMo_{12}H) with a tendency to predominance of the former band at higher temperatures [Fig. 5(2)–(7)]. At any treatment temperature, the spectrum depends on the duration [e.g. Fig. 5(3) and (4), Fig. 5(8) and (9)], showing that an equilibrium is never reached. Therefore, it is not possible to give the spectrum of the anhydrous acid: its existence could even be contested, owing to the continuous evolution of the spectra, rather consistent with mixtures of varying compositions (see below). A long treatment at 325°C for 90 h, [Fig. 5(9)] leads to a deep modification, related to a partial degradation of the polyanion.

Let us consider the evolution of the spectra in the region of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band. By assuming the stability of the 1-vanado-11-molybdophosphate anion (PMo_{11}V), the 1037 cm^{-1} band can be explained in terms of a splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band. However, this assumption implies a change in the direction of the splitting (low-frequency band at 1037 cm^{-1} , instead of an initial high-frequency band at 1072 cm^{-1}), which is rather surprising. The intensity increase of the 1037 cm^{-1} band with the temperature and duration of the thermal treatments is consistent with the progressive formation of another species, which implies the instability of PMo_{11}V , with a release of vanadium from the host structure. With this new assumption, mixtures of varying compositions are formed, in which the vanadium could be engaged in several species (e.g. PMo_{11}VH , V_2O_5 , vanadophosphates). The oxide V_2O_5 is unlikely to be responsible for the 1037 cm^{-1} band, taking into account its highest-frequency band

(1022 cm^{-1}) and its very low content (maximum 5% of the initial mass, i.e. undetectable in the IR spectrum). Note that in the Keggin-structure molybdo(tungsto)phosphates, the P content is very small (less than 2%), but the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band is surprisingly very intense. This enhancement of the intensity of a band which is expected to be weak, taking into account the low P content, is likely to be induced by the oxometallo framework surrounding the PO_4 tetrahedron. The high intensity of the band at 1037 cm^{-1} could be in favour of the existence of a species containing a PO_4 tetrahedron surrounded by an oxovanado framework. After moderate heatings (up to 190°C), the IR spectra are consistent with mixtures containing mainly PMo_{12}H (typical features of this compound are observed), the vanadophosphate species and polyoxomolybdates (there are not enough Mo centres released by the degradation of PMo_{11}V to give organized MoO_3). Exposure to water vapour at room temperature induces the disappearance of the 1037 cm^{-1} band, owing to the decomposition of the vanadophosphate species which may be unstable in the presence of water and may favour a reaction again giving PMo_{11}VH , but not quantitatively (the resulting spectrum is intermediary between that of PMo_{12}H and PMo_{11}VH , showing that PMo_{12}H formed during the heating process remains unchanged; see Table 4). After long thermal treatments at temperatures higher than 300 – 325°C , the mixtures undergo a deep transformation through irreversible decomposition, so that exposure to water at room temperature cannot induce a complete return to the Keggin structure [see Fig. 5(10)].

It appears, therefore, that heating for a long time in a dry atmosphere favours the degradation of PMo_{11}VH . The fragility of PMo_{11}VH is evidenced by these experiments, but also its reactivity and the ability of its degradation products to give a Keggin-structure compound after exposure to water vapour. It is clear that dehydration through temperature increase induces the decomposition of PMo_{11}VH . It would be interesting to perform heat treatments under wet oxygen flow, in order to study the effect of water vapour on the thermal stability of PMo_{11}VH .

Thermal Behaviour of PVW_{11}H from *In Situ* IR Study

The results obtained for PVW_{11}H on a ZnSe plate are shown in Fig. 6. Before any treatment [Fig. 6(1), Table 1] the IR spectrum is consistent with a Keggin structure compound: the perturbation introduced by the presence of vanadium is evidenced by the lowered symmetry of the PO_4 tetrahedron (two well separated bands at 1091 and 1067 cm^{-1}) and the decrease of the $\nu_{\text{as}}(\text{M}-\text{O}_d)$ frequency with respect to PW_{12}H (Table 1) (the $\nu_{\text{as}}(\text{M}-\text{O}_d)$ band includes motions of both $\text{W}-\text{O}_d$ and $\text{V}-\text{O}_d$ vibrators). After sweeping for 15 h under O_2 at room temperature, only a shoulder at 1090 cm^{-1} is visible on the side of the main maximum [Fig. 6(2)]. After thermal treatment at different temperatures under O_2 flow, the spectra resemble closely those of dehydrated PW_{12}H , with no splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band and the progressive development of a band at ca. 1030 cm^{-1} (the frequency is difficult to determine, because of overlap with $\nu_{\text{as}}\text{M}-\text{O}_d$) [Fig. 6(3)–(6)]. These spectra may be characteristic either of anhydrous PVW_{11}H or of a mixture of PW_{12}H and a vanadophosphate (characterized by the band at ca. 1030 cm^{-1}), the vanadium atom being released from the host structure, as in the case of PMo_{11}VH . The absence of splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band and the increase of the intensity of the 1030 cm^{-1} band (analogous with the intensity increase of the 1037 cm^{-1} band observed on heating of PMo_{11}VH) would rather favour the latter hypothesis. After treatments at higher temperatures (from 260 to 340°C) [Fig. 6(7)–(11)], some modifi-

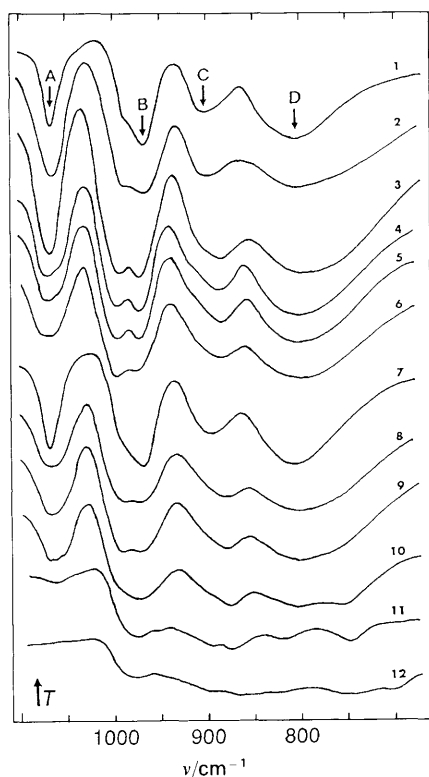


Fig. 6 IR spectra of PVW_{11}H (on a ZnSe plate) in the IR cell: all samples, except samples 1 and 12, are kept in dry oxygen atmosphere (treatments under oxygen flow). 1, Initial sample in air, prior to any treatment; 2, 15 h at room temperature; 3, 4 h at 200°C ; 4, 15 h at 200°C ; 5, 65 h at 200°C ; 6, 18 h at 235°C ; 7, 18 h at 260°C ; 8, 18 h at 300°C ; 9, 18 h at 315°C ; 10, 84 h at 315°C ; 11, 18 h at 340°C ; 12, sample 11 after exposure to air humidity. Bands: A, $\nu_{\text{as}}(\text{P}-\text{O}_a)$; B, $\nu_{\text{as}}(\text{M}-\text{O}_d)$; C, $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$; D, $\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$

cations progressively appear: a decrease of the intensity of the $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ band (near 900 cm^{-1}) and broadenings of all the other bands. After treatment at 340°C followed by exposure to water [Fig. 6(12), Table 4], the spectrum exhibits features of PW_{12}H , with poorly defined degradation products which induce a general broadening of the bands. From these experiments, we can conclude that PVW_{11}H is extremely fragile, and that the progressive elimination of the water molecules may favour the release of vanadium and the formation of PW_{12}H .

Conclusions

The evolution of the IR spectra of 12-molybdo- and 12-tungsto-phosphoric acids, PMo_{12}H and PW_{12}H , as a function of the temperature and the duration of the thermal treatments under dry oxygen flow reveals the presence of anhydrous acids which can be considered as protonated Keggin units uniformly distributed in the framework. PMo_{12}H , which does not resist long treatments at temperatures higher than 300°C under a dry atmosphere, is less stable than PW_{12}H .

The water of crystallization molecules play an important role in the stability of the related compounds containing vanadium, namely the 1-vanado-11-molybdo and 1-vanado-11-tungsto-phosphoric acids, PMo_{11}VH and PVW_{11}H : the evolution of the IR spectra as a function of the temperature and the duration of the thermal treatments under dry oxygen flow does not reveal the presence of anhydrous PMo_{11}VH (or PVW_{11}H). Dehydration induces a progressive decomposition with the release of vanadium from the host Keggin structure and the formation of PMo_{12}H (or PW_{12}H) and a

vanadophosphate species. Exposure to water vapour induces the decomposition of the latter (disappearance of a band at *ca.* $1037-1030\text{ cm}^{-1}$): the resulting IR spectrum is very similar to that of the parent Keggin-structure compound, namely PMo_{12}H or PW_{12}H , without splitting of the $\nu_{\text{as}}(\text{P}-\text{O}_a)$ band, which is characteristic of the substituted vanado compounds. A complete return to the initial state is never observed: even if PMo_{11}VH and, to a lesser extent, PVW_{11}H , are partly rebuilt, they are always mixed with PMo_{12}H or PW_{12}H , and some of the vanadium is necessarily out of the host Keggin structure. Moreover, PMo_{11}VH is more stable than PVW_{11}H .

These results are important for a better understanding of the chemical reactions which occur in the solid state during catalytic processes, especially in the $300-350^\circ\text{C}$ temperature range. In this range, if heating is conducted in a dry atmosphere, PMo_{12}H does not resist long treatments, PW_{12}H is stable, PMo_{11}VH and PVW_{11}H are no longer present and give rise essentially to the parent Keggin compounds PMo_{12}H and PW_{12}H and to a vanadophosphate species unstable in the presence of water. Although the water effect was proved to be kinetically unfavourable in oxydehydrogenating (ODH) reactions,^{4c,16} it would now be interesting to conduct experiments under a gas flow charged with water vapour, in order to check if the water vapour has a stabilizing effect on PMo_{11}VH and PVW_{11} and in this case, to determine the minimal water content required to obtain time-stabilized activity in ODH reactions.

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