FTIR investigation on Wells–Dawson and Keggin type heteropolyacids: dehydration and ethanol sorption

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Dedicated to Professor Józef Ziółkowski on the occasion of his 70th birthday.

Abstract

The FTIR spectra of Wells–Dawson and Keggin type heteropolyacids, $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$, respectively, were registered in the course of their dehydration at temperatures between room temperature and 300–350 °C as well as during the sorption of ethanol on dehydrated and and/or dehydroxylated samples. The changes on heating in the secondary structure of the samples were observed and discussed. Ethanol adsorbed on dehydrated heteropolyacid gets protonated and participates in the formation of secondary structure of heteropolyacid. In the case of dehydroxylated acids physical sorption of ethanol is only observed.
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1. Introduction

Heteropolyacids (HPA) and their salts are the object of steady interest both from the physico-chemical and catalytic point of view. They are active in a number of catalytic reactions in gas and liquid phase, redox as well as acid–base type. Since 1970s they have found successful application in several industrial processes and the number of publications concerning their properties does steadily increase. However, until now the study and application concerned predominantly HPAs, the anions of which exhibit the so-called Keggin structure. Their composition can be expressed by the formula $[X^{n+}M_{12}^{m+}O_{40}]^{(80-12m-n)-}$ (heteroatom X = P, As, Si, Ge, B, etc., polyatom M = W, Mo which may be substituted by V, Co, etc.). Much less attention has been given to another heteropolyacid structurally related to Keggin structure, so-called Wells–Dawson structure. Its physico-chemical and catalytic properties have been reviewed recently in [1]. The composition of its anion is expressed by the formula $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$. The Wells–Dawson structure may be derived from the Keggin one by the removing one M_3O_9 subunit from each of two Keggin anions and linking them by oxygen atoms thus forming a nearly ellipsoidal anion. The structures of both anions are presented in Fig. 1. Solid HPAs are strongly hydrated what results in the formation of the secondary structures composed of anions, protons or metal cations and water or other polar molecules.

Wells–Dawson HPAs are active in redox as well as in acid type catalytic reactions. In recent years the catalytic behaviour of the most frequently synthesised $H_6P_2W_{18}O_{62}$ (HP2W) was compared by several authors with that of $H_3PW_{12}O_{40}$ (HPW) using methyl *tert*-butyl ether (MTBE) formation from isobutene and methanol as the test reaction. In the gas phase the activity of the unsupported former was definitely higher than in the case of the latter one [2–5]. Still earlier higher activity of $H_6P_2W_{18}O_{62}$ and $H_6P_2Mo_{18}O_{62}$ than

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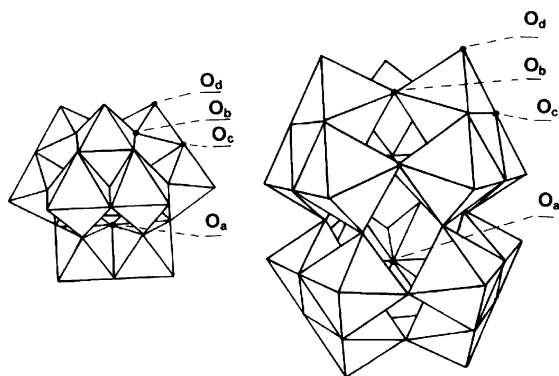*E-mail address:* lubanska@chemia.uj.edu.pl (A. Bielański).

Fig. 1. Keggin and Dawsona structures.

$H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, respectively, was observed in the liquid phase MTBE synthesis [6,7]. The higher activity of solid Wells–Dawson HPAs than that of Keggin ones contrasts with the fact that the order of acidities of both HPA types is reversed. Differential absorption heat of ammonia is equal to $150\,kJ\,mol^{-1}$ for $H_6P_2W_{18}O_{62}$ and $190\,kJ\,mol^{-1}$ for $H_3PW_{12}O_{40}$ [3], the value of Hammett Function H_0 is equal to -2.9 for HP2W and -3.6 for HPW [8]. Shikata et al. [3] explain the above inconsistency between the catalysis and acidity by assumption that it is the result of the differences in the secondary structure of both acids. These secondary structures were in the case of their experimental conditions (preheating temperatures 150 and 250 °C) crystalline in HPW and amorphous in HP2W. According to them the elliptical shape of the Wells–Dawson anions is not suitable for the formation of a stable crystalline secondary structure and leads to an amorphous and flexible one. Then the absorption–desorption has been easier and catalytic activity high, while the spherical shape of Keggin anion would favour a crystalline cubic structure, where absorption–desorption is slower and catalytic activity lower. To the similar conclusions concerning the role of secondary structure of $H_6P_2W_{18}O_{62}$ in MTBE formation arrived Baronetti and co-workers [9,10]. Their study has been carried out using the samples preheated in the larger range of temperatures than in [3]. The X-ray investigation has shown a decrease of unit cell volume on heating and also the differences in the relative intensities of the reflections from high Miller Index planes attributed to a disorder in the structure due to the water loss. These facts indicated the change in the secondary structure of the catalyst influencing its catalytic activity.

The present FTIR study of dehydration and sorption of ethanol on $H_6P_2W_{18}O_{62}$ as compared with the behaviour of $H_3PW_{12}O_{40}$ is a part of our investigation of a reaction similar to MTBE formation, namely the gas phase synthesis of ethyl-*tert*-butyl ether (ETBE) on $H_6P_2W_{18}O_{62}$ as the catalyst. The understanding of the mechanism of this latter reaction needs the knowledge of the interactions of particular reagents with the catalyst. The dehydration of both acids as well as the ethanol sorption are connected with the changes in the secondary structure due to the presence

of polar molecules, H_2O or C_2H_5OH in the pseudo–liquid phase. Due to their interactions with protons and HPA anions a system of hydrogen bonds, observed within the spectral range $4000–2000\,cm^{-1}$ or so, is forming [11,12] which was mostly not studied and discussed in the previous studies on heteropolyacids. The notable exception being the paper [13]. Hence, our study concerns the wide spectral range $4000–400\,cm^{-1}$ comprising both secondary ($4000–1200\,cm^{-1}$) and primary ($1200–400\,cm^{-1}$) structure of HPAs.

2. Experimental

The synthesis of $H_6P_2W_{18}O_{62}\cdot28.8H_2O$ sample prepared according to Baronetti et al. [9] has been described in [14]. The $H_3PW_{12}O_{40}$ sample (p.a.) was purchased from Aldrich Comp. The samples for FTIR investigations have been prepared at room temperature by directing a stream of water vapour onto about 10–15 mg of HPA placed at a silicon wafer. At these conditions both the absorbed and crystal water enable the formation of highly concentrated solution of the acid, which could be smeared over the surface of the wafer. In the open air and at room temperature HPA crystallized quickly giving a thin compact layer suitable for IR examination.

The IR cell situated in spectrometer chamber was connected with vacuum system. The sorption apparatus allowed heating the sample out of the spectrometer beam in vacuum or in controlled atmosphere. After heating the sample could be moved – without the contact with atmosphere – into the region of IR beam and sorption–desorption experiments carried out. Excalibur 3000 Series Digilab spectrometer was used.

3. Results and discussion

The study of ethanol sorption on HPAs has been preceded by the gradual dehydration of the samples under vacuum. This process has been controlled by FTIR measurements. The information then obtained characterises in some measure the changes in the secondary structure of HPA. The exact amount of water of crystallisation in the sample could not be determined by this technique. A sample of Wells–Dawson type HPA $H_6P_2W_{18}O_{62}$ kept at room temperature over saturated $Mg(NO_3)_2$ solution contained $28.8H_2O$ molecules per mole of HPA. Similarly the formula of $H_3PW_{12}O_{40}\cdot19H_2O$ has been found corresponding to Keggin type HPA sample. TG/DTA analysis of hydrated HP2W carried out in helium stream at atmospheric pressure showed, that on heating the sample by $5\,°C\,min^{-1}$ it has begun to loose water already at room temperature during the period of the derivatograph flushing with helium gas. The dehydration rate reached the maximum at about 70 °C. The anhydrous HP2W did not change its weight up to about 230 °C. Above 250 °C dehydroxylation process (departure of so called water of constitution) was observed, reaching maximal rate at 300 °C. In

the case of Keggin type HPW TG/DTA analysis two-stage mode of crystallisation water removing was observed with the maxima of dehydration rate at 63 and 172 °C. Anhydrous sample was reached at 220 °C and the dehydroxylation process occurred above 300 °C.

3.1. Dehydration of $H_6P_2W_{18}O_{62}$

In the present case of very thin layer of the sample dehydrated under vacuum the high degree of dehydration could be obtained even at temperature close to room temperature. Anhydrous HP2W was obtained after evacuation at 100 °C.

The spectrum of fresh hydrated sample is shown in Fig. 2A(a) and B(a). Within 4000–1200 cm^{-1} region a broad band at 3500 cm^{-1} is seen characteristic of hydrogen bonded water molecules. It is accompanied by bands at 1705 cm^{-1} and 1620 cm^{-1}. The former is ascribed to hydroxonium ion H_3O^+ or $H_5O_2^+$ δ vibration [15] and the latter to δ vibration of the non protonated water molecules. The spectrum characteristic of Wells–Dawson structure, of $P_2W_{18}O_{62}^{6-}$ anion, is situated in the 1200–400 cm^{-1} range (Fig. 2B(a)). In accordance with the literature [16] it comprises the following bands: 1090 cm^{-1} ascribed to ν_{as} (P–O_a) vibration, 961 cm^{-1} characteristic of ν_{as} (W=O_d) vibration between terminal O_d atoms and W atoms, as well as 908 and 773 band ascribed to ν_{as} chain vibrations in which O_b and O_c atoms participate, W–O_b–W and W–O_c–W, respectively.

As it is shown by the spectra presented in Fig. 2A(a–c) distinct changes in the region 4000–1200 cm^{-1} are observed on gradual evacuation of the sample at room temperature. First of all the shift of 3500 cm^{-1} band to the lower frequencies is observed. According to Ratajczak et al. [12] a consensus has been reached in the recent years that shift of such bonds to lower frequencies may be generated mainly by mechanical anharmonic coupling between the high frequency ν (XH) and low frequency ν_s (XHY) and δ (XHY)/ν (XHY) vibrational modes of the hydrogen bond X–H$\cdots$Y. As subtraction spectra in Fig. 2C show the shift is realized by the vanishing of certain bands with maxima at about 3550 cm^{-1} during first evacuation when the pressure dropped to 1 Tr and about 3470 cm^{-1} during further evacuation at room temperature. This corresponds to the gradual removing of water molecules most loosely hydrogen bonded and remaining gradually of more strongly bonded ones. Simultaneously faster decrease of about 1620 cm^{-1} band of more loosely bonded not protonated H_2O species is observed than that of 1705 cm^{-1} hydroxonium ion.

After 10 min of evacuation at room temperature three maxima not very distinct could be observed between 3400 and 2200 cm^{-1} (Fig. 2A(c)). The subtraction spectrum in Fig. 2C(c-b) clearly shows that at these conditions a triplet appears with maxima at about 2960, 2390 and 2200 cm^{-1}. According to Ratajczak et al. [12] such structures appear in the case of medium strong and strong hydrogen bonds and are due to the Fermi resonance between ν (XH) stretching mode and some other internal modes. The appearance of

triplet is accompanied by the further removing of the hydrogen bonded water of crystallisation and decrease of the bands of H_3O^+ and non protonated H_2O species. However, the spectrum in Fig. 2A(c) shows that the removing of the both latter species after 10 min of evacuation at room temperature was not complete. The removing of them has been realized only after evacuation at 100 °C for 10 min (Fig. 2A(d)). The subtraction spectrum in Fig. 2C(d-c) shows remaining of the 2385 and about 2200 cm^{-1} components of the triplet during evacuation at 100 °C and further departure of the rest of water to which the vibrations in 1700–1600 cm^{-1} region and 3410 cm^{-1} were characteristic.

Let us now observe that the characteristic triplet appears at the moment when nearly all (evacuation at room temperature only) or practically all (evacuation at 100 °C) of water molecules were given off (Fig. 2C(d-c)). In the hydrated sample the HPA anions were bonded in the secondary structure [1] by the intermediation of H_2O molecules forming a number of hydrogen bonds to which broad band shifting on dehydration from 3500 to 3370 cm^{-1} is ascribed. After departure of water of crystallisation the bonds between the anions have to be effectuated mostly by the immediate hydrogen bonds between neighbouring HPA anions. The fact that triplet is shifted still more strongly towards the lower frequencies indicates that such intermolecular hydrogen bonds in the dehydrated HPA are definitely stronger than the bonds effectuated by the intermediation of water molecules forming water of crystallisation.

The dehydration also results in some changes in the spectral region corresponding to the skeletal vibrations of HPA anions. As Fig. 2B shows the bands at 1090 and 773 cm^{-1} in which O_a and O_c oxygen atoms are involved practically do not change their position. On the other hand, the vibrations at 961 and 908 cm^{-1} decrease at the cost of growing new bands of 990 and 935 cm^{-1}. This indicates that terminal oxygen atoms O_d of Wells–Dawson structure in the former case and doubly coordinated oxygen atoms O_b (in W–O_b–W chains) interact most strongly in the system of hydrogen bonds existing in the hydrated sample and on dehydration change their frequencies indicating new type of interactions.

The HP2W sample has been next heated and evacuated at 200 °C for 15 min. The band at about 3000 cm^{-1} was still present, the bands about 1700–1600 cm^{-1}, present at room temperature, vanished completely (Fig. 2A and B(e)). No essential changes were observed in the anion vibrations region. Hence, it could be concluded that the sample was completely devoid of crystal water but no dehydroxylation took place which would influence the skeleton vibrations. The bands about 3000 cm^{-1} corresponded to immediate hydrogen bonds between Wells–Dawson anions.

However, the distinct changes in the skeleton vibrations were registered after the sample has been evacuated at 300 °C for 15 min (Fig. 2B(f)). The vanishing of the 900 cm^{-1} band as well as the shifts of the other bands indicated a destruction of the anion structure. These circumstances may suggest that it is O_b atom in W–O_b–W chain joining W_3O_{13} subunits
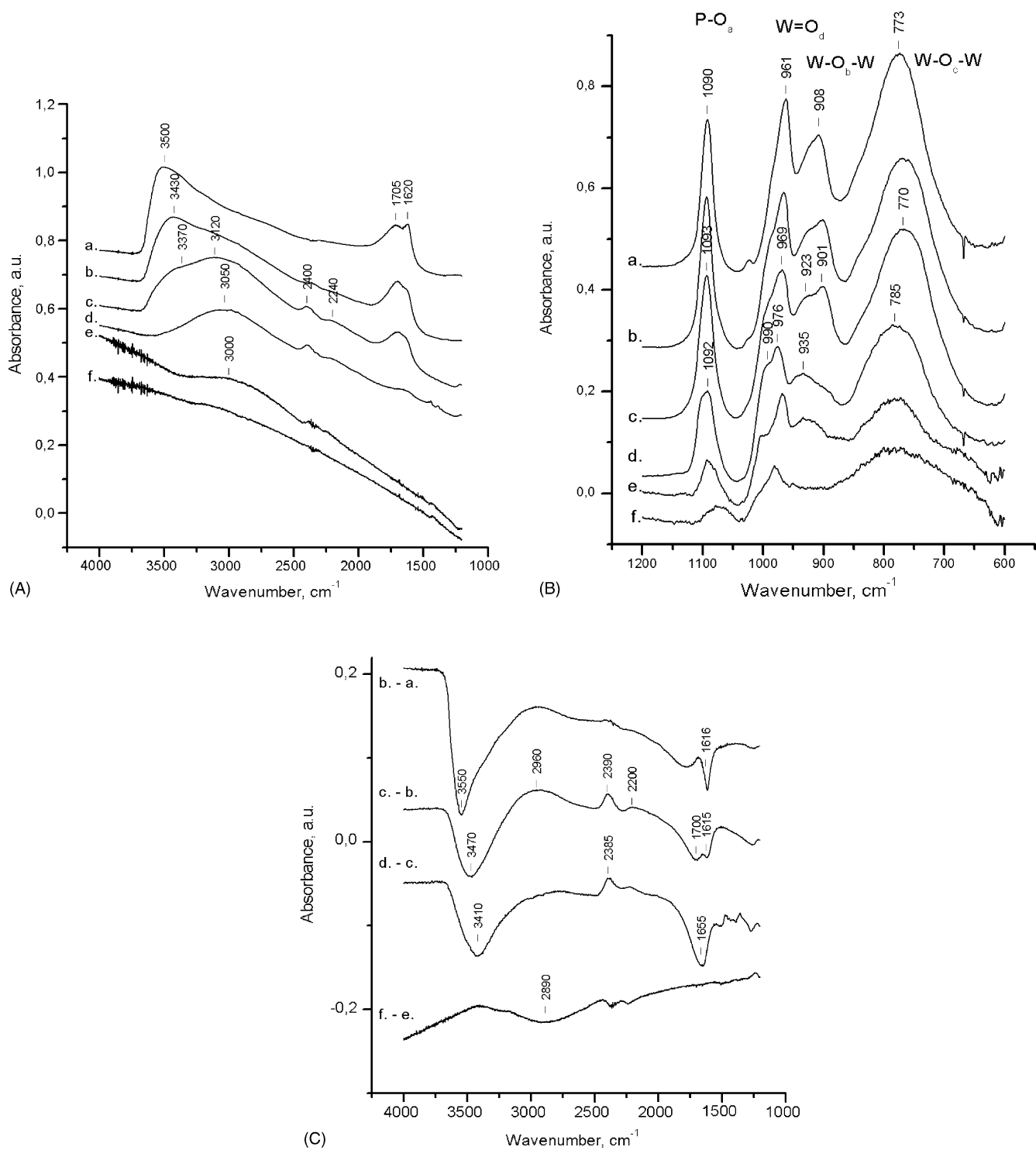
Fig. 2. Dehydration of $H_6P_2W_{18}O_{62}$; FTIR spectra: (A) secondary structure 4000–1200 cm^{-1}; (B) Wells–Dawson (primary) structure 1200–600 cm^{-1}; (C) subtracted spectra: (a) hydrated HP2W, (b) dehydration at pressure of 1 Tr at 20 °C, (c) evacuation at 20 °C, 10 min, (d) evacuation at 100 °C, 10 min, (e) evacuation at 200 °C, 15 min, (f) evacuation at 300 °C, 15 min, (b-a) dehydration of pristine sample, (c-b) evacuation at room temperature, (d-c) evacuation in temperature range between 20 and 100 °C, and (f-e) evacuation in temperature range between 200 and 300 °C.
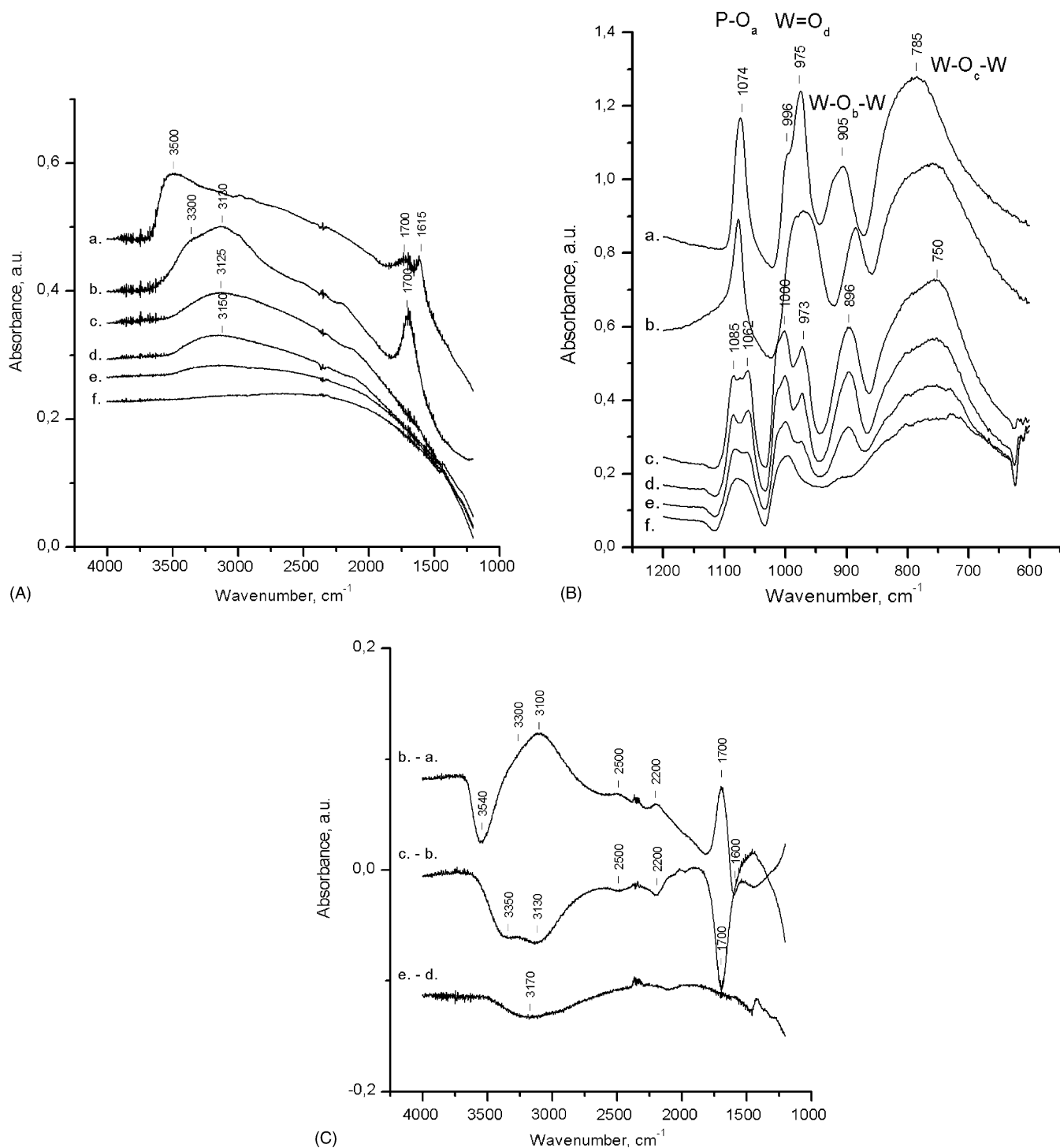
Fig. 3. Dehydration of $H_3PW_{12}O_{40}$; FTIR spectra: (A) secondary structure 4000–1200 cm^{-1}; (B) Keggin (primary) structure 1200–600 cm^{-1}; (C) subtracted spectra: (a) hydrated HPW, (b) evacuation at 20 °C, 10 min, (c) evacuation at 100 °C, 10 min, (d) evacuation at 200 °C, 10 min, (e) evacuation at 300 °C, 10 min, (f) evacuation at 350 °C, 10 min, (b-a) dehydration and evacuation of pristine sample at room temperature, (c-b) evacuation in temperature range between 20 and 100 °C, (e-d) evacuation in temperature range between 200 and 300 °C.

which is extracted on the departure of the water of constitution in the dehydroxylation process.

3.2. Dehydration of $H_3PW_{12}O_{40}$

Sample of Keggin type HPA $H_3PW_{12}O_{40}$ has shown somewhat different behaviour than that of Wells–Dawson type HPA during dehydration at room temperature. Just after the deposition on the silicon wafer the spectrum of the hydrated sample showed a broad band at about $3500\,cm^{-1}$ typical for hydrogen bonded water molecules as well as bands $1615\,cm^{-1}$ ($\delta(H_2O)$) and $1700\,cm^{-1}$ ($\delta(H_3O^+)$ or $\delta(H_5O_2^+)$) (Fig. 3A and B(a)). All bands characteristic for Keggin anion within the region of structural vibrations were observed: $1074\,cm^{-1}$ ascribed to ν_{as} (P–O$_a$) vibration, $975\,cm^{-1}$ typical of ν_{as} (W=O$_d$) vibration, and 905 and $785\,cm^{-1}$ bands of ν_{as} W–O$_b$–W and W–O$_c$–W chain vibrations, respectively. The sample left in open air losses most of water of crystallisation even without evacuation what was signalled by the vanishing of the band at about $3500\,cm^{-1}$ and appearance of a new broad band with maxima at about 3300 and $3130\,cm^{-1}$. Simultaneously, the deformation band of non protonated water at $1615\,cm^{-1}$ vanished and the intensity of a hydroxonium ion $1700\,cm^{-1}$ increased thus indicating partial at least protonation of loosely bonded neutral water molecules (Fig. 3A(b)). Gradual outgasing and further evacuation at room temperature only slightly changed the spectrum.

The subtraction spectrum of outgased and hydrated sample (Fig. 3C(b-a)) shows that dehydration process at room temperature results in removing of some part of most loosely bonded water, while significant amount of hydrogen bonded water characterized by the new band about $3100\,cm^{-1}$ is remaining in the secondary structure. Moreover, this strong broad band $3100\,cm^{-1}$ appeared to be one component of the hydrogen bonds triplet. Two other very weak components are situated at about 2500 and $2200\,cm^{-1}$.

Subsequent evacuation at $100\,°C$ results in complete removing of the bands about 1700 and $1620\,cm^{-1}$, i.e. departure of protonated and not protonated water molecules forming water of crystallisation (Fig. 3A(c)). At this stage, only broad band about $3125\,cm^{-1}$ remains in the $4000–1200\,cm^{-1}$ region. This band shifted to $3150\,cm^{-1}$ after heating to $200\,°C$ has to be ascribed to the hydrogen bond between neighbouring Keggin anions. It vanishes completely on heating to $350\,°C$ as the result of HPA dehydroxylation (Fig. 3A(f)).

Upon the dehydration of $H_3PW_{12}O_{40}\cdot aq$ sample its spectrum within anion structural vibrations $1200–600\,cm^{-1}$ suffers a series of quite distinct changes (Fig. 3B). After the treatment in vacuum at $100\,°C$ the intensity of ν_{as} (P–O$_a$) at $1074\,cm^{-1}$ decreased and simultaneously two bands appeared in its immediate vicinity, one with somewhat higher frequency $1085\,cm^{-1}$ and one with somewhat lower one $1062\,cm^{-1}$. The latter corresponds to $1065\,cm^{-1}$ peak observed in the doublet by Essayem et al. [13]. On heating to

200 and $300\,°C$ the central peak vanishes and only the doublet remains. Splitting of ν_{as} (W=O$_d$) band at $975\,cm^{-1}$ (in pristine sample) is simultaneously observed. In the hydrated state it exhibited only a weak shoulder at $996\,cm^{-1}$ which on heating to $100\,°C$ and to higher temperatures grew larger and shifted to $1000\,cm^{-1}$.
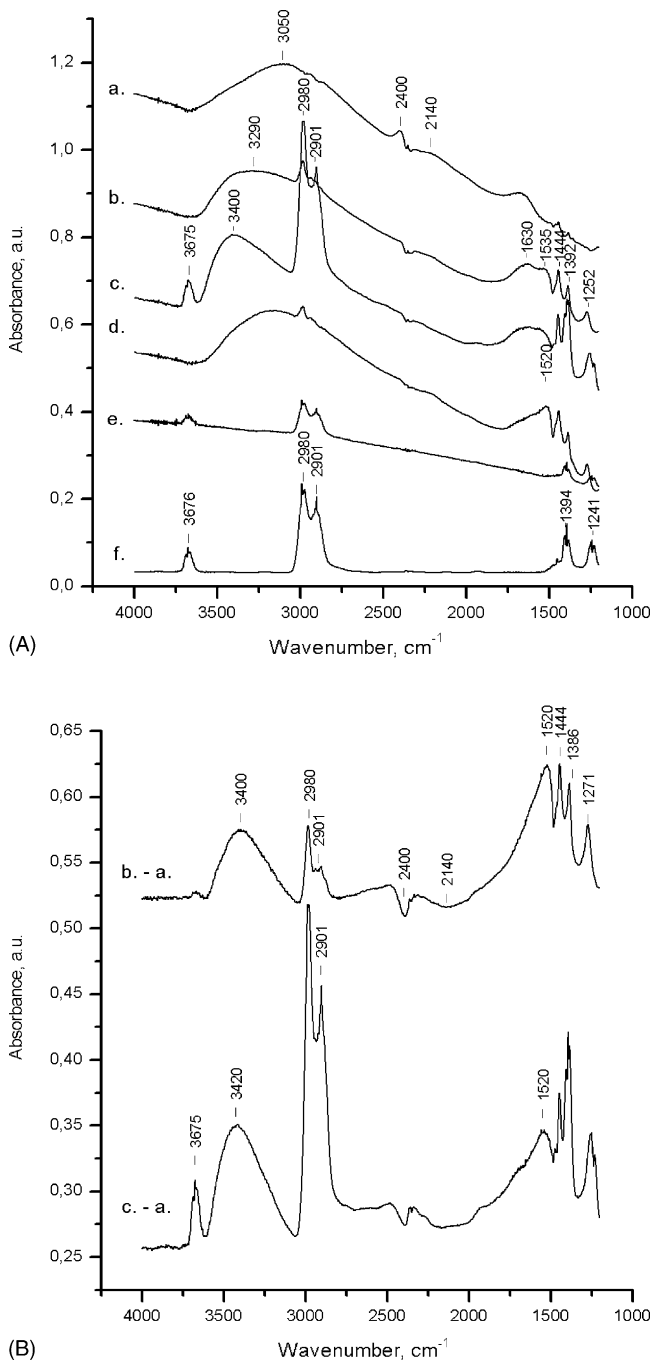

Fig. 4. Ethanol sorption on dehydrated $H_6P_2W_{18}O_{62}$ (A); subtracted spectra (B): (a) sample evacuated at $100\,°C$, 10 min, (b) sorption of EtOH 0.8 Tr at $20\,°C$, (c) sorption of excess of EtOH (5 Tr) at $20\,°C$, (d) desorption of EtOH 20 min at $20\,°C$, (e) sorption of EtOH 0.8 Tr at $20\,°C$ on sample dehydroxylated at $300\,°C$, (f), spectrum EtOH in gas phase, (b-a) sorption of 0.8 Tr, (c-a) excess of EtOH.

Table 1
The position of main structural vibrations in Wells–Dawson and Keggin type anions (cm^{-1})

	$H_3PW_{12}O_{40}$		$H_6P_2W_{18}O_{62}$	
	Hydrated	Dehydrated at 100 °C	Hydrated	Dehydrated at 100 °C
ν_{as} (P—O$_a$)	1074	1085 (1074), 1062	1090	1092
ν_{as} (W=O$_d$)	975 (996 sh)	1000, 973	961	990, 976
ν_{as} (W—O$_b$—W)	905	896	908 (920 sh)	935
ν_{as} (W—O$_c$—W)	785	750	773	785

On the other hand, the other structural vibrations of the anion suffer only minor changes. The ν (W—O$_b$—W) band of the frequency 905 cm^{-1} in the case of pristine sample shifted only to 896 cm^{-1} in the case of heating of the sample at 200 or 300 °C. Similarly the broad band ν (W—O$_c$—W) with flat maximum at about 785 cm^{-1} shifted to about 750 cm^{-1}.

All these facts indicate that the most sensitive to the changes in the primary structure of $H_3PW_{12}O_{40}$ due to the different content of crystal water are the ν (P—O$_a$) and ν (W=O$_d$) modes. All these changes occur in parallel with the departure of hydrogen bonded water (vanishing of bands around 3500–3300 cm^{-1}) and vanishing of protonated water clusters (1700 cm^{-1}). Hence, it is believed that their interpretation should be done in common as the result of water of crystallization departure.

Let us observe that with gradual weakening of the ν (W=O$_d$) vibration at 975 cm^{-1} growing on its cost the shoulder at 1000 cm^{-1} increases to a distinct and strong band (Fig. 3B(c)). Similar band was also observed in [13] and also in the case of $H_3PMo_{12}O_{40}$ [17] and $H_4SiW_{12}O_{40}$ [15] and has been attributed to the change introduced by the sample dehydration. In hydrated sample terminal O$_d$ oxygen atom is involved in a hydrogen bond with protonated water cluster [18]. On dehydration the latter bond is disrupted and O$_d$ oxygen atom becomes "free" or more probably is forming of an OH group active in the formation of hydrogen bond with a neighbouring Keggin anion.

According to [13] protonation of O$_d$ atom results in the lowering of the symmetry of the W_3O_{13} subgroups thus modifying the bond energy of one of the central P—O$_a$ bonds in the anion. These authors also observe that the low frequency shift is consistent with a weakening of P—O$_a$ bond as a result of a general withdrawal of electrons towards the incoming proton. Such effects were also confirmed in the present investigations in which the formation 1085/1062 cm^{-1} doublet was observed in the dehydrated samples accompanying the vanishing of the single 1074 cm^{-1} peak.

3.3. Ethanol sorption

Let us now discuss the spectrum of ethanol adsorbed on the sample of $H_6P_2W_{18}O_{62}$ Wells–Dawson type heteropolyacid dehydrated at 100 °C (Fig. 4A). The effect observed after the introduction of the first portion of EtOH vapour under the pressure of 0.8 Tr is shown in Fig. 4A(b). As

Fig. 4B (subtraction spectra) shows a new band appeared at about 3400 cm^{-1} which is accompanied by the distinct decrease of bands: 2400 cm^{-1} and a very broad one about 2140 cm^{-1}. The last ones are the components of the triplet mentioned in the previous section. The decrease of its third component at about 3000 cm^{-1} cannot be excluded despite that simultaneously a number of new bands characteristic of ethanol molecules appeared at the "valley" in this region of the subtraction spectrum. These new bands 2980 and 2901 cm^{-1} are characteristic for the symmetric and asymmetric stretching vibrations of the —CH$_3$ and —CH$_2$— groups of EtOH.

The weakening of the triplet indicates the decrease of the amount of hydrogen bonds joining HPA anions, the latter being now separated by hydrogen bonded EtOH molecules playing the same role as the water molecules forming the "water of crystallisation". It seems justified to ascribe them the new broad band at 3400 cm^{-1} in analogy to the band around 3500 cm^{-1} in hydrated $H_6P_2W_{18}O_{62}$.

In the spectral region 1800–1200 cm^{-1} adsorbed ethanol exhibits several bands most of which are analogous to those observed by Highfield and Moffat [19] in the case of ethanol sorption on $H_3PW_{12}O_{40}$. In particular we observed the appearance of ca. 1520 cm^{-1} band which has been ascribed in [19] to asymmetric δ (C—OH) deformation vibration in ethoxonium ion $C_2H_5OH_2^+$, the vibration which we suggest to be similar to that of H_3O^+ ion at 1705 cm^{-1}. Moreover, the bands at 1444 and 1386 cm^{-1} have been ascribed by us to the asymmetric and symmetric deformations of —CH$_3$, respectively.

Entirely different spectrum of EtOH adsorbed on $H_6P_2W_{18}O_{62}$ activated at 300 °C was obtained (Fig. 4A(e)). In this case only the bands characteristic of non protonated ethanol were observed: 2980 and 2901 cm^{-1} characteristic of ν_{as} and ν_{sym} of —CH$_2$ and —CH$_3$ groups, 3675 cm^{-1} of OH groups in the EtOH molecule as well as 1394, 1241 and 1066 cm^{-1} corresponding to the same bands in gas phase C_2H_5OH. The absence of the broad band of hydrogen bonded ethanol at about 3420 cm^{-1} as well as 1520 cm^{-1} of protonated ethanol $C_2H_5OH_2^+$ indicates also the absence of Brönsted acid sites being the result of heteropolyacid dehydroxylation at 300 °C.

Ethanol sorption on dehydrated $H_3PW_{12}O_{40}$ Keggin type heteropolyacid occurred similarly as it was observed in the case of Wells–Dawson type one. The introduction of EtOH resulted in the appearing of similar bands. However,

EtOH sorption on Keggin type HPA proceeds much slower than it was observed in the case of Wells–Dawson type HPA. In contrast with Wells–Dawson type HPA in the case of Keggin type sample activated at $300\,^{\circ}C$ the bands at 1510, 1444, 1383 and $1263\,cm^{-1}$ characteristic for ethanol chemisorbed on Brönsted acid were still registered and it was necessary to heat the sample up to $350\,^{\circ}C$ in order to obtain spectrum of ethanol sorbed on dehydroxylated $H_3PW_{12}O_{40}$.

The differences in the behaviour of both investigated heteropolyacids during ethanol sorption are understood as the result of differences in secondary structures containing Wells–Dawson or Keggin type anions.

4. Conclusions

When comparing the IR spectra of Keggin and Wells–Dawson heteropolyacids within the structural vibration region we observe – despite the distinct similarities – also the differences in the positions of analogous vibrations both in hydrated and dehydrated state (Table 1). First of all the $P-O_a$ bond in Keggin anion characterizes by lower frequency and hence is weaker and more sensitive to the hydration state (splitting on dehydration) than that in the case of Wells–Dawson anion the vibration of which remains unchanged on dehydration.

In both cases, the highest sensitivity to dehydration is exhibited by the ν ($W=O_d$) and ν ($W-O_b-W$) modes. The former one in both heteropolyacids exhibits characteristic splitting on dehydration the mechanism of which has been discussed in a previous section.

The spectrum of Keggin acid dehydrated at $100\,^{\circ}C$ remains in the structural vibrations region essentially unchanged after heating at 200 and $300\,^{\circ}C$ and it is necessary to heat the sample up to $350\,^{\circ}C$ in order to register almost complete vanishing of the $905\,cm^{-1}$ band ($W-O_b-W$) indicating presumably the rupture of the bonds between W_3O_{13} structural subunits. The thermal stability of Wells–Dawson acid is lower. The intensity of all structural bands decreases already after heating the sample at $200\,^{\circ}C$, the spectrum obtained after heating at $300\,^{\circ}C$ seems to indicate to almost complete collapse of anion structure.

It is interesting to compare the frequency of hydrogen bond triplets formed in secondary structures of both type heteropolyacids (Figs. 2C(c-b) and 3C(b-a)). In the case of Wells–Dawson type HPA one may observe triplet of bands at about 2960, 2390 and $2200\,cm^{-1}$, while in the Keggin type HPA these bands are characterised by the frequencies 3100, 2500 and $2200\,cm^{-1}$. Generally, positions of the peaks of hydrogen bonds in the case of $H_6P_2W_{18}O_{62}$ are more strongly shifted towards lower frequency, thus indicating stronger bonds in the secondary structure. This may possibly be the hydrogen bond between HPA anions or hydrogen bonds due to the presence of the rest of water still remaining in the sample.

The other difference between Wells–Dawson and Keggin type heteropolyacids is appearance of the band $1700\,cm^{-1}$ typical for hydroxonium ion. This band gradually vanishes during the dehydration of $H_6P_2W_{18}O_{62}$ at room temperature, while in the case of Keggin type HPA its dehydration results in the distinct increase of this band. This effect may be explained as the privileged hydroxonium ion formation in the secondary structure containing Keggin units. The above mentioned TG/DTA experiments seem to confirm such interpretation. Dihydrate of HPW is stable at temperatures up to $170\,^{\circ}C$ while no such hydrate is formed by HP2W.

Sorption of ethanol on dehydrated $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$ leads to qualitatively identical results indicating protonation of C_2H_5OH molecules and the formation of secondary structure involving ethoxonium ions creating hydrogen bonds between HPA anions. On the other hand, sorption of ethanol on the dehydroxylated HPA samples seems to correspond rather to physical adsorption. The effects are weaker and no protonated species appear.

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