Thermal transformations of α-$H_6P_2Mo_{18}O_{62} \cdot nH_2O$ heteropolyacid

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According to the ^{31}P NMR spectroscopy, heteropolyacid (HPA) $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ (P_2Mo_{18}), α-isomer of the Dawson structure, transforms upon heating above 80 °C partially (up to 30%) to γ-isomer, in which both polar groups Mo_3O_{13} of the heteropolyanion are turned by 60° around the C_3 axis, and partially to β-isomer in which only one group is turned. The β- and γ-isomers of P_2Mo_{18} have been found for the first time. Their transformation into the α-isomer occurs upon rehydration in one week in air and in 1 h in an aqueous solution. HPA P_2Mo_{18} decomposes on heating up to 350 °C to HPA $H_3PMo_{12}O_{40}$ (PMo_{12}) and a previously unknown phase of the $HPMo_6O_{21}$ composition, which in its turn decomposes at ~375 °C to molybdenyl phosphates and MoO_3. The PMo_{12} decomposition occurs *via* two routes to form the same products at temperatures of ~400 and 450 °C with corresponding exotherms of MoO_3 crystallization.

Key words: heteropolyacid, thermolysis, ^{31}P NMR spectroscopy, thermogravimetric analysis.

Studies of the thermal stability of heteropolyacids (HPA) of molybdenum and tungsten and their thermal conversions are of a special interest for elucidation of the HPA nature as well as their use, particularly in catalysis.[1,2] Thermal transformations of HPA $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ (P_2Mo_{18}) known as the α-isomer with the Dawson structure (Fig. 1, *a*)[3,4] have been studied by DTA as well as by IR and ^1H NMR spectroscopies.[5] Dehydration and partial decomposition of the HPA were found in the temperature range of 120—300 °C. The $H_6P_2Mo_{18}O_{62} \cdot 3H_2O$ phase with nonhydrated protons formed at 270 °C. A non-identified structural change was found upon further heating along with crystallization at 530 °C to form MoO_3, likely together with the phosphate admixture. The IR-spectroscopic study[6] suggested the P_2Mo_{18} decomposition through the HPA $H_3PMo_{12}O_{40}$ (PMo_{12}) intermediate with the Keggin structure, which decomposes at $T \geq 400$ °C.[7]

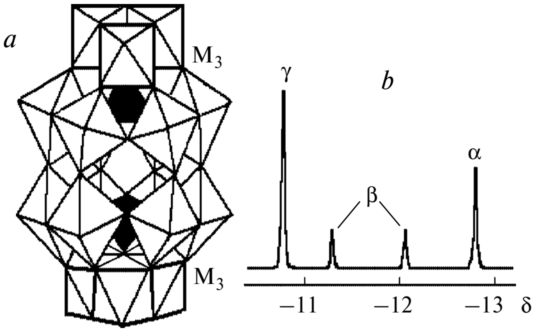

Fig. 1. *a*. A model of the α-$P_2M_{18}O_{62}{}^{6-}$ heteropolyanion (M = Mo, W) (inside M—O frame there are two PO_4 tetrahedra; M_3 are the polar caps containing three edge-sharing MO_6 octahedra. When they rotate, the HPA isomers are formed.). *b*. The ^{31}P NMR spectrum of aqueous solution of the HPA $H_6P_2W_{18}O_{62} \cdot nH_2O$ containing a mixture of α-, β-, and γ-isomers after thermal treatment at 150 °C.

The ^{31}P NMR spectroscopy was not used earlier to study HPA P_2Mo_{18} thermolysis. Meanwhile, this method allows one to observe and identify the phosphorus-containing phases that form on heating the P—Mo- and P—W-HPAs and cannot be revealed by other techniques. It has been found for a tungsten analog, α-$H_6P_2W_{18}O_{62}$ (P_2W_{18}), that the solid-state α→γ isomerization of the heteropolyanion occurs at $T > 100$ °C when its both polar groups W_3O_{13} ("triplets") (see Fig. 1, *a*) rotate by 60° around the third order axis with the resulting γ-isomer undergoing further thermal conversions.[8]

In this work, the thermal transformations of HPA P_2Mo_{18} were studied by DTA as well as by ^{31}P NMR and IR spectroscopies.

Experimental

Heteropolyacid $H_6P_2Mo_{18}O_{62} \cdot 23.5H_2O$ was prepared by electrodialysis of a solution of Na_2MoO_4 and H_3PO_4 (Mo : P = 9) according to an earlier described procedure.[9] According to the ^{31}P NMR spectroscopy data, the concentration of P_2Mo_{18} in the sample was at least 97% (Table 1).

The DTA and TGA data were obtained on a Q-1500 D derivatograph (MOM) at a heating rate of 10 °C · min^{-1}. Samples

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Table 1. Attribution of some peaks in the ^{31}P NMR spectra of solutions of P—Mo- and P—W-HPAs

Anion of HPA	$\delta_P \pm 0.03$	Reference
$PW_{12}O_{40}{}^{3-}$	−15.07	10, 11
α-$P_2W_{18}O_{62}{}^{6-}$	−12.83	4, 8, 11
β-$P_2W_{18}O_{62}{}^{6-}$	−12.1, −11.3	4, 8, 11
γ-$P_2W_{18}O_{62}{}^{6-}$	−10.8	8
$PMo_{12}O_{40}{}^{3-}$	−3.65	12, 11
α-$P_2Mo_{18}O_{62}{}^{6-}$	−2.95	4, 11
β-$P_2Mo_{18}O_{62}{}^{6-}$	−2.47, −1.97	—*
γ-$P_2Mo_{18}O_{62}{}^{6-}$	−1.53	—*

* The data of this work.

are denoted according to the heating temperature; for instance, HPA-300 corresponds to heating up to 300 °C. The HPA samples for NMR and IR measurements were prepared by isothermal heating in a derivatograph normally for 1 h. The IR spectra were measured with a Specord 75 IR spectrometer in KBr pellets. The ^{31}P NMR (MAS) spectra of solid samples were recorded using a CXP-300 Bruker spectrometer (121.47 MHz) with a standard 7 mm Bruker probe with sweep widths of 10 and 50 KHz and a rotation rate of 3—4 KHz. The pulse width and the interpulse delay were 5 μs and 30 s, respectively. The ^{31}P NMR spectra of solutions were measured with an MSL-400 Bruker spectrometer (161.98 MHz) with a 5 KHz sweep width, a 12 μs pulse width, and a 20 s interpulse delay. Chemical shifts (δ) are given relative to 85% H_3PO_4 with taking into account the correction for the magnetic susceptibility difference.

Results and Discussion

Heteropolyanion P_2Mo_{18} containing two equivalent P atoms (see Fig. 1, *a*) exhibits in solution a single ^{31}P NMR peak like the similar anion α-P_2W_{18} but in a different δ range (see Table 1). In the P_2W_{18} β-isomer, one of the polar triplets is turned by 60° around the C_3 axis resulting in non-equivalency of the P atoms in two halves of the anion. As a consequence, this isomer in a solution exhibits two peaks with equal intensity shifted downfield relative to the signal of the α-isomer (see Fig. 1, *b*). Since both triplets in the γ-isomer are turned, it gives one peak shifted still more downfield. As a result, the ^{31}P NMR spectra of solutions containing a mixture of three isomers of P_2W_{18} exhibit four peaks (see Fig. 1, *b*). For P_2Mo_{18} the β- and γ-isomers have not been observed earlier. As in the case of P_2W_{18},[8] one could expect their formation upon thermal treatment of the initial HPA α-P_2Mo_{18}.

Figure 2 presents the ^{31}P NMR (MAS) spectra of the HPA P_2Mo_{18} solid samples after thermal treatment under different regimes. The spectrum of the initial HPA contains two close signals **A** (see Fig. 2) due to the presence of the P_2Mo_{18} anions in unequal crystallographic positions.[13] Upon heating up to 300 °C, the **A** peaks are broadened and shifted downfield. The samples retain complete solubility in water (20 °C). When the samples are stored in air with a humidity of 50—70%, the peaks shift backwards within a few hours except for peak **B** (δ −1.6), which disappears in a few days only. The HPA PMo_{12} admixture, which is noticeable in the initial P_2Mo_{18} samples as a narrow line **C** (δ −3.6, ~50 Hz), increases with an increase in the calcination temperature. According to the spectral data, HPA-300 contains the initial HPA P_2Mo_{18} and PMo_{12}, but the sample dissolves more slowly and not completely. In the spectrum of HPA-350, the peak PMo_{12} (**C**) remains and peak **D** with the width of ~1000 Hz and δ −6 appears (see Fig. 2). The intensity ratio is $I_C : I_D \approx 1$. The peaks **C** and **E** (~1400 Hz, δ −7) in the ~1 : 1 ratio are seen in the spectrum of HPA-380. Above 400 °C (see Fig. 2), the spectra contain mainly peak **E** with strong spinning sidebands and are similar to the earlier described[7,12,14] spectra of molybdenyl phosphates formed upon the HPA PMo_{12} thermolysis. The samples HPA-350—600 partially dissolve in water, and the sample HPA-400 dissolves completely upon boiling. The HPA samples prepared by heating above 400 °C partially dissolve upon boiling until the molar ratio Mo : P ≈ 6 is achieved, which is typical of a simple mixture of MoO_3 and H_3PO_4.[12]

Reversible changes in the ^{31}P NMR spectra found after heating phosphorus-containing HPAs at temperatures up to 300 °C are usually due to variation in the degree of interaction between protons and the anion during dehydration.[7,8,15] As known,[16] protons in the HPA crystallohydrates enter the composition of the oxonium ions $H_5O_2{}^+$, and each of them is bound uniformly with several neighboring heteropolyanions by rather weak hydrogen bonds. After HPA dehydration, the oxonium ions decompose and the heteropolyanions are protonated, which results in a downfield shift of the HPA signal in the ^{31}P NMR spectra. In the presence of water vapor, the oxonium ions are regenerated and the initial spectra are recovered, as was found for the HPA P_2Mo_{18} heated below 300 °C (see Fig. 2). For oxonium regeneration, it is sufficient to store the preheated HPA at a relative humidity of ~50% for 24 h. However, not all changes in the spectra caused by P_2Mo_{18} calcination disappear for this time.

In the ^{31}P NMR spectra of water-dioxane (1 : 1) solutions prepared immediately after heating the samples, the peaks of the initial HPA α-P_2Mo_{18} and PMo_{12} are seen along with three peaks from unknown P—Mo complexes (Fig. 3). This spectrum is completely similar to that of a mixed solution of the α-, β-, and γ-isomers of P_2W_{18} in terms of the intensity ratios and peak positions (see Fig. 1, *b*). Similarly, the new P—Mo complexes corresponding to the β- and γ-isomers in the position and intensity are converted into the α-isomer with time. This makes it possible to attribute three new peaks (see Fig. 3, Table 1). Complete transformation of β- and γ-P_2Mo_{18} to α-P_2Mo_{18} occurs in 1 h in an aqueous solution and in one day in a water—dioxane mixture. The P_2Mo_{18} isomers

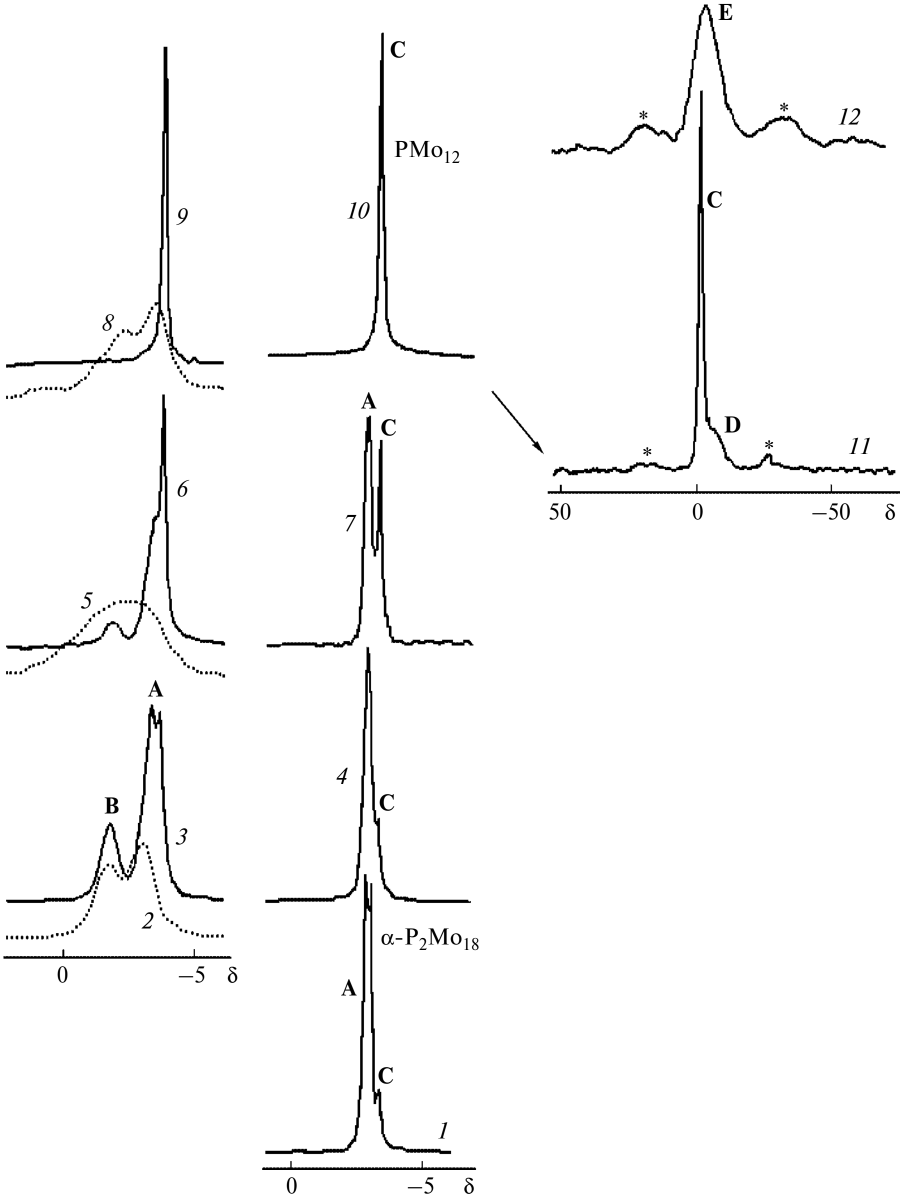


Fig. 2. The ^{31}P NMR (MAS) spectra of the initial HPA $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ (20 °C) (*1*) and heated for 1 h at 150 (*2*, *3*, *4*), 300 (*5*, *6*, *7*), 350 (*8*, *9*, *10*, *11*), and 500 °C (*12*) immediately after heating (*2*, *5*, *8*), in 24 h (*3*, *6*, *9*) and in 7 days (*4*, *7*, *10*, *11*). The spectrum widths are 10 (*1—10*) and 50 kHz (*11, 12*). The sidebands because of the sample rotation are designated by «*» .

were likely not found earlier because of their short lifetime in solutions. In the solid phase this transformation occurs more slowly (in about a week), when the sample is stored in air at the 50—70% humidity. In the absence of water vapor, in sealed ampules, the γ- and β-isomers of P_2Mo_{18} remain unchanged for at least a month. In all the cases, the reconversion of P_2Mo_{18} to α-isomer occurs more rapidly than that of P_2W_{18} under similar conditions.[8] This corresponds to higher lability of the P_2Mo_{18} anion observed earlier in solutions by comparing the rates of the oxygen isotope exchange of the P_2Mo_{18} and P_2W_{18} HPA anions with water.[4] It was found that only polar triplets M_3O_{10} (see Fig. 1, *a*) of both heteropolyanions participate in the exchange with a solution and therefore are the most labile fragments. Protonation of the M—O—M bridges between the triplets and the anion framework weakens additionally their bonds favoring rotation of the triplets, which was found during the thermal dehydration of both P_2W_{18} and P_2Mo_{18}.

The compositions of the HPA samples after thermal treatment were determined from the ^{31}P NMR spectra of as-prepared water—dioxane solutions. The concentration of the γ-isomer estimated from the ^{31}P NMR spectra of these solutions correlates with the intensity of the **B** line

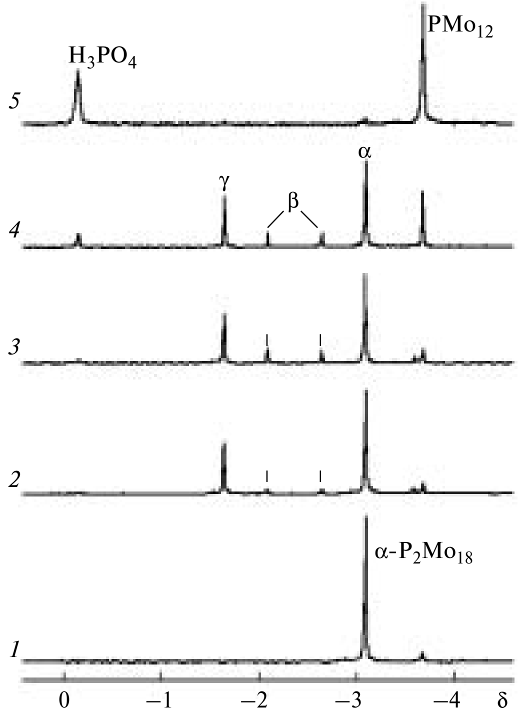


Fig. 3. The ^{31}P NMR spectra of water—dioxane (1 : 1) solutions of the initial HPA $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ (*1*) and HPA heated for 1 h at 150 (*2*), 200 (*3*), 300 (*4*), and 350 °C (*5*).

in the solid phase spectrum (see Fig. 2), and this permits the assignment of this line to the γ-isomer. According to the spectra, the solid-state α→γ isomerization begins already at 80 °C and is accelerated with a temperature increase. After heating for 1 h at 150 °C, the fraction of the γ-isomer is ~30% and does not increase with heating duration, but the fractions of the β-isomer and PMo_{12} increase (in 7 h ~10% and 5%, respectively). The PMo_{12} fraction after heating for 7 h at 300 °C was ~40%.

The step-by-step dissolution, as it has been done in the study of PMo_{12} thermolysis,[7,12] reveals that HPA-300 contains components, which dissolve either fast or slowly. In the first water extract obtained during 1—3 min, all the isomers of P_2Mo_{18} prevail and PMo_{12} appears. Fast dissolution points to the presence of P_2Mo_{18} and PMo_{12} in the form of HPA. The second water extract was obtained after 3 h of the suspension stirring, and it contained mainly α-P_2Mo_{18} along with PMo_{12}. After complete dissolution of the precipitate, its composition was nearly the same. Since P_2Mo_{18} cannot be formed repeatedly under these conditions, this fact means that a poorly soluble form of P_2Mo_{18}, likely its anhydride, is present in the precipitate (the anhydride of P_2W_{18} is insoluble at all)[8]. By analogy with P_2W_{18}, one can assume that during thermolysis, the γ-isomer first transforms to anhydride, but it is impossible to confirm this by the spectrum, because the γ-isomer has time to convert completely into α-species during slow dissolution. The HPA-350 sample contains the PMo_{12} phase (detectable by the **C** line, see Fig. 2) and the P_2Mo_{18} admixture. Hence, P_2Mo_{18} is virtually absent from this sample, even in the form of anhydride, and the broad line is due to another phase formed from P_2Mo_{18} simultaneously with PMo_{12}.

The DTA data made possible the more precise determination of the temperature ranges and the nature of the transformations found by NMR. On the DTA curve (Fig. 4), one can see three endotherms at 140, 180, and 235 °C, which are due to HPA dehydration, the endotherm at 320 °C, the exotherms at 385, 405 (the most intense), and 450 °C, as well as the endotherm at 755 °C. The latter is due to the melting of MoO_3 at the temperature lower than that of pure MoO_3 (801 °C)[17] because of the admixture of phosphate in the oxide phase. According to TGA, one can conclude that after removal of the hydrate water, the partial anhydride $H_4P_2Mo_{18}O_{61}$ forms with the endotherm at ~235 °C and the corresponding weight loss (Scheme 1). This transformation occurs also during storage of the sample for 3 h at 210 °C.

The $H_4P_2Mo_{18}O_{61}$ anhydride decomposes completely to the HPA PMo_{12} (line **C**) and some residue (line **D**), which is characterized by the endotherm at 320 °C. It follows from the intensity ratio for these lines ($I_C : I_D \approx 1$)

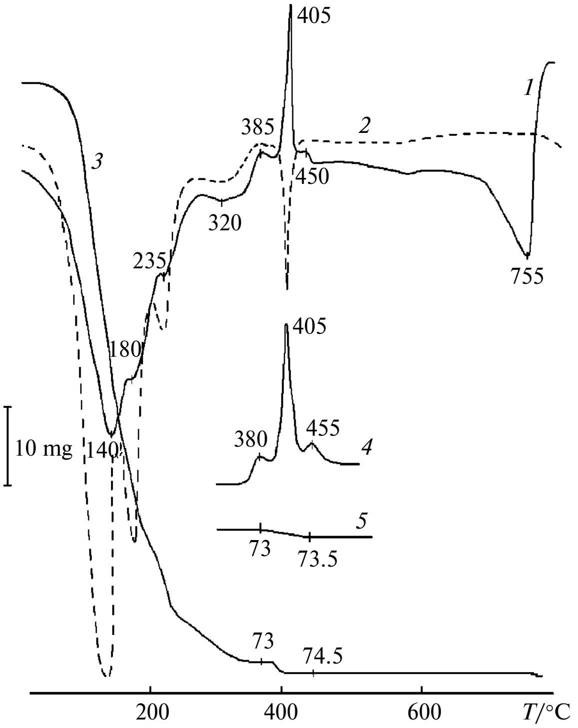
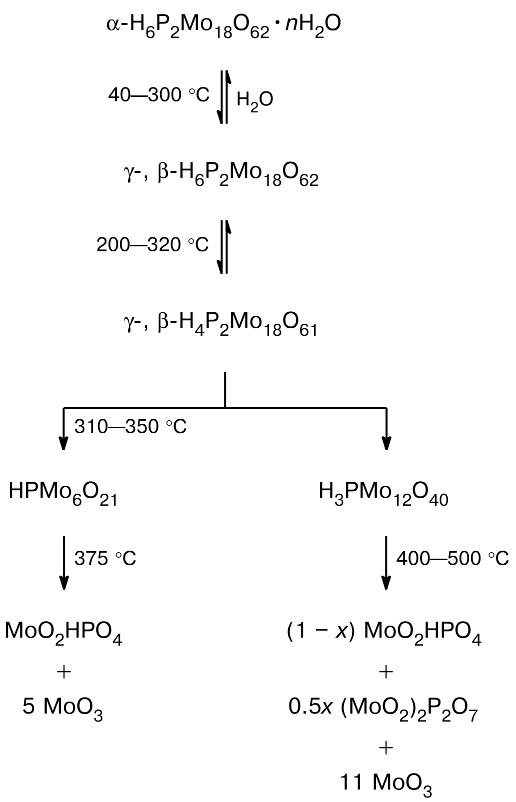


Fig. 4. The DTA (*1*), DTG (*2*), and TGA (*3*) curves for the sample $H_6P_2Mo_{18}O_{62} \cdot 23.5H_2O$ (weighed portion 500 mg) in dynamic regime and after isothermal treatment at 310 °C for 200 min (DTA (*4*), TGA (*5*)). The weight loss (in mg) is shown on curves *3* and *5*.

Scheme 1



in the ^{31}P NMR (MAS) spectrum of the solid sample heated at 350 °C (see Fig. 2) that phosphorus of the initial HPA is equally distributed between PMo_{12} and the residue according to the following equation

$$H_4P_2Mo_{18}O_{61} \longrightarrow H_3PMo_{12}O_{40} + HPMo_6O_{21}. \qquad (1)$$

The reaction also proceeds completely upon heating the sample for 3 h at 310 °C. One could expect that the decomposition of the PMo_6 residue to MoO_2HPO_4 and MoO_3 occurs immediately upon the evolution of PMo_{12} from P_2Mo_{18}. However, according to the XRD data, this sample contains no MoO_3 and is completely soluble, whereas only peaks of PMo_{12} and H_3PO_4 are present in the ~3 : 1 ratio in the spectrum of the sample in the water—dioxane mixture. The data obtained provide evidence that the P—Mo phase of the above composition actually exists and when dissolved it gives PMo_{12} according to the reaction

$$2\,HPMo_6O_{21} + 2\,H_2O \longrightarrow H_3PMo_{12}O_{40} + H_3PO_4. \qquad (2)$$

The PMo_6 phase retains in the sample as such up to ~375 °C and then decomposes (see Scheme 1) as can be seen from the exotherm of the MoO_3 crystallization (380 °C) and the appearance of the MoO_2HPO_4 peak in the ^{31}P MAS-NMR spectrum.

The phase of HPA PMo_{12} decomposes independently of the PMo_6 phase. A part of structural water is lost at 380 °C and anhydride *1* [12] is formed

$$H_3PMo_{12}O_{40} \longrightarrow HPMo_{12}O_{39} + H_2O\uparrow \qquad (3)$$

with the weight loss determined by TGA, which is equivalent to a loss of one H_2O molecule. Near 400 °C anhydride *1* transforms *via* two routes

$$HPMo_{12}O_{39} \longrightarrow MoO_2HPO_4 + 11\,MoO_3, \qquad (4)$$

$$2\,HPMo_{12}O_{39} \longrightarrow$$
$$\longrightarrow [PMo_{12}O_{38}{}^{+}][PMo_{12}O_{39}{}^{-}] + H_2O\uparrow. \qquad (5)$$

Route (4) gives the second exotherm (~405 °C) on the DTA curve corresponding to MoO_3 crystallization, and route (5) occurring through complete anhydride *2* is characterized by the weight loss.[12] Above 450 °C anhydride *2* decomposes.

$$[PMo_{12}O_{38}][PMo_{12}O_{39}] \longrightarrow$$
$$\longrightarrow (MoO_2)_2(P_2O_7) + 22\,MoO_3 \qquad (6)$$

The third exotherm on the DTA curve (~455 °C) is due to the crystallization of a new portion of MoO_3. The ratio between routes (4) and (5) for PMo_{12} decomposition and the temperature of the latter exotherm depend on the thermal treatment protocol[14] and likely the presence of other phases and admixtures. The route described by Eq. (4) prevailed for the samples under study. During nonisothermal heating, the boundaries of transformations shift and overlap.

As a whole, the IR spectra confirm the conclusion on the conversion of the HPA P_2Mo_{18} to HPA PMo_{12}. The spectrum of P_2Mo_{18}-350 is close to that of the HPA PMo_{12} [18] in the position of the absorption bands and their intensities. The differences are due to superposition with the spectrum of the new phase. After heating at 400 °C, the IR spectrum is a result of the superposition of the PMo_{12} and MoO_3 spectra, and after heating at 500 °C, the IR spectrum resembles that of MoO_3. After heating above 600 °C, some additional weak bands typical of Mo and W pyrophosphates[19] are observed in a range of 1000—1150 cm^{-1}.

On the basis of the above data, the thermal conversions of the HPA α-P_2Mo_{18} can be presented by Scheme 1 in which the transformations of the HPA PMo_{12} described by Eqs. (3)—(6) are summarized.

Hence, new important data on the thermolysis of the HPA α-P_2Mo_{18} were found by the ^{31}P NMR spectroscopy. Before the formation of the first partial anhydride (in the 240—300 °C range), the process occurs similarly to that with the HPA α-P_2W_{18}. The thermal dehydration results in the protonation of the HPA anion by the inherent protons at the bridging O atoms between the polar triplets and equatorial fragment of the anion, facilitating the conversion to γ- and β-isomers. The following step, the abstraction of the O atoms of the anion by the protons to form the first partial anhydride $H_4P_2Mo_{18}O_{61}$, likely with the structure of the γ-isomer, occurs at the temperature ~100 °C lower than that for P_2W_{18}. In the case of P_2W_{18}, the anion is preserved even after the loss of the second O atom (>500 °C), and it decomposes to the mixed oxide phase only upon the removal of the third O atom in the 600—650 °C, *i.e.*, at higher temperature than that of the decomposition of the HPA $H_3PW_{12}O_{40}$ anion (~500 °C).[10] The framework of the P_2Mo_{18} anion endures a loss of only one O atom and then decomposes completely with a minor increase in temperature (up to ~320 °C) to the HPA PMo_{12} and an unknown compound, which has the $HPMo_6O_{21}$ composition according to the reaction equation and exists in a narrow temperature range (~320—370 °C).

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