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# KINETICS AND MECHANISM OF DEHYDRATION OF HETEROPOLYACIDS

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## Abstract

The kinetics and mechanism of the dehydration and decomposition of heteropolyacids of molybdenum, tungsten and vanadium ($H_{3+x}Y^{x+}M_{12}O_{40}\cdot mH_2O$; $Y$=Si, P; $M$=Mo, W) were studied. The data obtained on the dehydration kinetic parameters correlate with the expected structures, of these crystal hydrates, the IR data and X-ray phase analysis.

**Keywords:** decomposition, dehydration, kinetics

## Introduction

The prospects for the wide use of the crystalline heteropolyacids (HPAs) are due to their catalytic activity, proton conductivity and thermal stability [1]. These important features are observed at relatively high temperatures. Thus, for the use of HPAs in practice, detailed information should be available on the thermal stability, with quantitative characteristics of their dehydration and decomposition.

## Experimental

### *Materials*

The initial HPA reagents, with the common formula $H_{3+x}Y^{x+}M_{12}O_{40}\cdot mH_2O$ ($Y$=Si, P; $M$=Mo, W; $m$=0–31; $x$=degree of central atom oxidation) were recrystallized and purified from saturated aqueous solutions. Vanadium HPAs $H_{3+n}PMo_{12-n}V_nO_{40}\cdot mH_2O$ ($n$=1–3) were synthesized according to literature method [2]. The compositions of the compounds obtained were established by dissolution of the HPA samples in $D_2O$, followed by elemental and X-ray phase analyses and identification via the IR and Raman spectra. Deuteration was

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achieved by water distillation in vacuum. The treatment was repeated a number of times. As the HPAs are strong acids and easily dissociated into ions, proton exchange by deuterium takes place in full. Complete deuteration was controlled by NMR and IR methods.

### *Apparatus*

Thermoanalytical investigations were conducted under dynamic and quasi-isothermal conditions with a derivatograph (MOM) in air. The sample mass was 0.1–0.2 g. Kinetic studies were carried out under non-isothermal conditions according to two independent versions. The first version involved use of a plate crucible derivatograph to ensure dehydration at a maximum surface with minimum layer thickness. The second version involved a flow reactor with no diffusion braking, ensuring the minimum contribution of back-reaction. The experimental data were compared. In the determination of kinetic parameters, the thermoanalytical curves relating to mass loss and gas isolation were used.

The flow reactor design is described in [3]. IR spectra were recorded on a Specord-75 IR provided with a thermoset which allows spectrum recording in the temperature range 20–250°C. The heating rate was the same in TG, DTG and DTA experiments. LiF or $CaF_2$ was used to make final samples in the form of a tablet.

X-ray diffractograms were obtained on a Dron-2.0 diffractometer, with $CuK_\alpha$ radiation.

## Results and discussion

Crystalhydrate stability is usually determined on proton aqua complexes and the mode of their decomposition [4]. The dehydration of HPA samples with high water contents ($m$=29–31) comprises several stages, with the rapid loss of more than 50% of the water during the first stage. Even quasi-isothermal conditions do not allow an estimation of the temperature range of stability of the intermediate phase. This suggests the slight association of some water molecules in the HPA hydrates with high water contents with the anion and the formation of an independent framework.

The initial stages of the thermal dehydration of the PHAs do not differ from the processes of ice sublimation or water vaporization. It is impossible to identify the intermediates of these transformations, which might be connected with the similar kinetic stabilities of the initial and intermediate phases and parallel-consecutive reactions of dehydration and decomposition of the crystal hydrate phases.

For the tungsten HPAs, two stable phases are formed after the first stage of dehydration, containing 14 and 6 water molecules per molecule of the acid phase.

In contrast with the tungsten HPAs, the molybdenum HPAs have the second and third stages of dehydration slightly divided. These can be separated under quasi-isothermal conditions. On the whole, the water molecules are interdependent rather than depending on the $O_{HPA}$ atoms. However, some quite short contacts $O_{HPA}\cdots O_{H_2O}$, equal in length to hydrogen-bonds, stabilize the structure. The HPA crystal hydrates are therefore more stable in air than those with high water contents. The dehydration process is reversible; it takes place on the surface and moves towards the centre of the spherical nucleus. Accordingly, in order to allow more specific conclusions about the kinetics, a prior evaluation of the most obvious reaction mechanism was undertaken according to Satava [5]. For this purpose, a linear function of the temperature integral $\log g(\alpha)$ was plotted *vs.* $1/T$ for five different mechanisms of solid-phase reactions, including nucleation, interphase boundary movement and diffusion. Analysis of the data showed that in HPA dehydration with a transformation degree of $\alpha\geq0.05$–$0.55$, the rate-limiting process is a chemical reaction at the phase boundary. It is described by the topochemical equation of a contracting sphere with reaction order 2/3. The deviation from a linear dependence at $\alpha\geq0.55$ is connected with a change in the solid-phase reaction mechanism. During dehydration the HPA structure shrinks, this process being regulated by the anions as they come together. It becomes difficult to remove water from the resulting surface. In this case, the rate is determined by the diffusion of water molecules through the product layer. Thus, kinetic analysis cannot be performed here. Nucleation at a low transformation degree is insignificant. It coincides with the solid body processes, as the dehydration mechanism can hardly be described by the topochemical equation alone.

To establish the kinetic parameters the Coats-Redfern integral method [6] was applied, using the reaction order obtained by the Satava method. Kinetic analysis of the TG curve for a transformation degree $\alpha=0.05$–$050$ reveals the linear dependence on $1/T$. This proves the topochemical mechanism determined with the Satava method.

To treat the isolated gas curves obtained in the continuous flow reactor, the computer program TA IB [3] was used. The linearity of $\log g(\alpha)$ *vs.* $1/T$ was tested for 13 different mechanisms for solid-phase reactions. The analysis demonstrated that the dehydration in the conversion range $\alpha=0.05$–$0.65$ was best described by the equation of a contracting sphere. This confirms the data obtained by TG, DTG and DTA.

The kinetic parameters for the HPA dehydrations investigated with the two different versions are presented in Table 1. The difference between the data does not exceed ±8%.

The activation energy and exponential factor correlate reasonably with the structural ideas on the HPA crystal hydrates [7]. Via these structures, it is easy to explain the removal of the weakly bound ‘tunnel’ water between the anions. The $O_{H_2O}\cdots O_{HPA}$ bond length is 2.9–3.44 Å. The removal of water molecules coordinated to the HPA atoms leads to increased kinetic parameters. The $O_{H_2O}\cdots O_{HPA}$ bond length for low-water HPAs is 2.3–2.5 Å, which indicates the strong stability of the bonding of the HPA with the water molecules.

**Table 1** Kinetic parameters of HPA dehydration

| HPA | $E_1$/ kJ mol$^{-1}$ | $E_2$ der./fl. react | log$A_2$ | $E_3$ | log$A_3$ |
|---|---|---|---|---|---|
| $H_4SiW_{12}O_{40}\cdot 30H_2O$ | 12–24 | 75.2/80.2 | 4.8/10.4 | 120.6/124.4 | 11.2/12.9 |
| $H_3PW_{12}O_{40}\cdot 29H_2O$ | 12–24 | 87.6/96.8 | 4.9/12.7 | 143.6/156.7 | 11.5/16.2 |
| $H_3PMo_{12}O_{40}\cdot 31H_2O$ | 12–24 | 66.8/– | 4.6/– | 86.0/– | 16.9/– |
| $H_4SiMo_{12}O_{40}\cdot 31H_2O$ | 12–24 | 59.8/– | 4.9/– | 79.3/– | 18.8/– |
| $H_4PMo_{11}VO_{40}\cdot 31H_2O$ | 12–24 | 50.0/– | 4.6/– | 65.0/– | 10.7/– |
| $H_5PMo_{10}V_2O_{40}\cdot 31H_2O$ | 12–24 | 50.0/– | 4.5/– | 65.0/– | 10.5/– |
| $H_6PMo_9V_3O_{40}\cdot 31H_2O$ | 12–24 | 46.4/– | 4.4/– | 60.4/– | 9.9/– |

The kinetic results on HPA dehydration were confirmed by the findings from X-ray phase analysis and IR spectroscopy. The elementary cell volume decreased sharply during the dehydration process, e.g.

$H_3PW_{12}O_{40}\cdot 29H_2O$, $V$=12600.54 Å$^3$;

$H_3PW_{12}O_{40}\cdot 14H_2O$, $V$=3159.59 Å$^3$;

$H_3PW_{12}O_{40}\cdot 6H_2O$, $V$=1953.12 Å$^3$.

As the anions come together, coordinate bonds are formed with water molecules, which changes the whole system of hydrogen-bonds. The new bonds are formed between outer sphere protons and hydroxylanions.

The IR spectra of the HPAs were studied in a thermocell. The double structure of the water molecules (deformational vibrations at 1660 and 1720 cm$^{-1}$) was clearly seen for the initial samples of HPA crystal hydrates. A broad absorption band with an isolated maximum was observed in the region of the OH valent vibrations, at 3380 and 3550 cm$^{-1}$, with a shoulder at 3180 cm$^{-1}$.

On heating, the intensities of the absorption bands at 1660, 3380 and 3550 cm$^{-1}$ decreased sharply, while the absorption bands relating to $H_5O_2^+$ at 1720 and 3180 cm$^{-1}$ remain unchanged [8]. This also suggests a more stable character of the water molecules bound in the low-water HPAs.

Isotope substitution was applied to distinguish the stage limiting the rate of HPA thermal decomposition. The primary isotope effect in the reactions involving the limiting stage of proton transfer was caused by the sharp energy of the zero vibrations and was determined by the activation energy increase. The difference $E_D-E_H$ was approximately 6 kJ mol$^{-1}$.

TG, DTG and DTA analysis indicated that complete H–D substitution led to a temperature increase for the maximum reaction rate in all stages of water removal. The *E* values obtained were 6–15 kJ $mol^{-1}$ higher for the deuteroacids. The results point to the important role of proton transfer in the stage of crystal water removal. Experimental methods are described in detail in [9].

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