DTA AND TG ANALYSIS OF HETEROPOLYACIDS OF THE SERIES $H_{(3+x)}PMo_{(12-x)}V_xO_{40} \cdot nH_2O$

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DTA, TG and DTG of molybdovanadophosphoric acids of the series $H_{(3+x)}Mo_{(12-x)}V_xO_{40} \cdot nH_2O$ ($x = 0, 1, 2, 3$) were carried out. The samples with the highest content of water of crystallization ($n = 19$–34) fuse above 40 °C, giving solutions of heteropolyacids which boil at 110 to 130 °C. The total loss of crystallization water occurs below 170–200 °C. The anhydrous acids decompose (dehydroxylation) at temperatures decreasing from the average value of 433 °C for $x = 0$ to about 293 °C for $x = 3$. For these vanadium-containing samples, an exothermic peak not accompanied by weight change appears at about 450, 430 and 390 °C for $x = 1, 2$ and 3, respectively, indicating a transformation in the solid state. If $x = 0$, a weaker endothermic effect of dehydroxylation overlaps with a stronger exothermic effect, and only one exothermic effect exists, at 435 °C.

The catalytic properties of heteropolyacids (HPA) and their salts are of increasing interest, due to the fact that they are strong solid acids and, in some cases at least, also exhibit redox properties. Owing to their specific structure, in which the complex anions, usually of molecular weight above 1700 (Keggin units), are not interbonded and in hydrated form are separated by strongly solvated cations; small polar molecules such as CH_3OH and C_2H_5OH can easily penetrate into the bulk of the crystallites and thereby enter into immediate contact with the catalytically active internal centres, similarly as occurs in zeolites [1]. The catalytic behaviour of $H_3PMo_{12}O_{40}$ or $H_4SiMo_{12}O_{40}$ is considered to depend in some measure on the pretreatment of the samples, which controlls the amount of water molecules contained between the complex anions and also, in the case of heating at sufficiently high temperature, may result in the degradation of the HPA into the component oxides MoO_3 and P_2O_5 or SiO_2. This is why a knowledge of the thermal behaviour of the HPA and their salts is important from the point of view of catalysis.

It has been shown that in the series of isomorphic dodecaheteropoly acids $H_3PX_{12}O_{40}$ or $H_4SiX_{12}O_{40}$, in which $X = $ Mo or W, variation of the peripheral
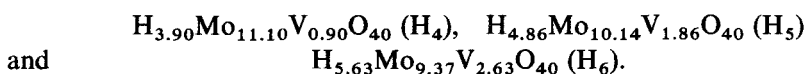
elements (X) in the complex anion strongly influences such properties as thermal stability [2] and catalytic activity [3, 4]. In the present research, it was decided to study the effects of peripheral elements by gradually substituting Mo atoms by V atoms in dodecamolybdophosphoric acid, i.e. to study the series of samples with compositions given by the formula $H_{(3+x)}PMo_{(12-x)}V_xO_{40} \cdot nH_2O$ (x = 0, 1, 2 or 3). The present paper deals with the thermal behaviour of these HPA; only the first compound of the series, i.e. $H_3PMo_{12}O_{40}$, has been investigated previously [2, 5–8].

Experimental

12-Molybdophosphoric acid, $H_3PMo_{12}O_{40}$ (designated as H_3), was obtained via the method described by Tsigdinos [8], by boiling MoO_3 with a solution of H_3PO_4, concentrating the solution by evaporation and cooling; a yellow precipitate was formed. The latter was purified by recrystallization from water.

Molybdovanadophosphoric acids $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$ and $H_6PMo_9V_3O_{40}$ (designated as H_4, H_5 and H_6) were obtained according to Tsigdinos and Hallada [9] by mixing appropriate amounts of an acidified aqueous solution of Na_2HPO_4 and $NaVO_3$ with a solution of Na_2MoO_4. The HPA were then extracted with ethyl ether. In this extraction, a heteropolyetherate was present as a middle layer. After separation, a stream of air was passed through the heteropolyetherate to free it of ether. The solid was dissolved in a small amount of water and the solution was concentrated by evaporation over dried molecular sieve. The orange (x = 1) to deep-red (x = 3) precipitate was purified by recrystallizing it twice more in the same way.

The atomic ratio Mo/V for the samples was determined by X-ray microanalysis; a series of V_2O_5–MoO_3 samples obtained by fusion of the oxides were used as standards to obtain the calibration curve. The analytical results indicated that the compositions of the vanadium-containing samples corresponded to the following formulae:

$$H_{3.90}Mo_{11.10}V_{0.90}O_{40} \ (H_4), \quad H_{4.86}Mo_{10.14}V_{1.86}O_{40} \ (H_5)$$
and $$H_{5.63}Mo_{9.37}V_{2.63}O_{40} \ (H_6).$$

The HPA preparations were stored in a desiccator over a saturated solution of NaCl in order to obtain a constant concentration of water of crystallization. Some samples were also dried at room temperatute in a stream of dry air or nitrogen for 24 h.

Thermogravimetric investigation of the HPA samples was carried out with a Mettler Thermoanalyser TA–2. Samples of about 50 mg were introduced into a

small corundum crucible 8 mm in diameter. α-Al_2O_3 was used as the standard substance for thermal analysis.

The results relating to the amount of "water of constitution", i.e. the water considered to be bonded in the form of acid OH groups, were compared with the results of ammonia chemisorption. The latter investigation was carried out in a constant pressure apparatus in which the changes in the volume of the gas phase were measured. The samples were outgassed in vacuum, first for 1 h at room temperature and then at temperatures of 150–180°, chosen so as to obtain full removal of the water of crystallization without marked decomposition of the anhydrous acid (temperature of point A in Fig. 1). The adsorption of ammonia was carried out at 50° and 100 Torr. At the same temperature, the samples were then evacuated and ammonia was again adsorbed. The difference between the amount of ammonia adsorbed in the two cases was taken as the amount of NH_3 chemisorption, assuming that the second step involved only physical adsorption.
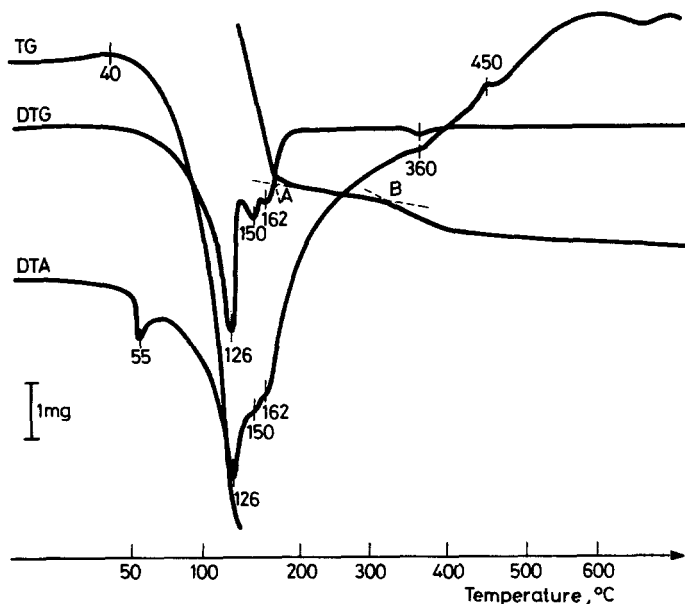

Fig. 1 Thermal curves of sample H_4/I ($H_{5.63}PMo_{9.37}V_{2.63}O_{40}$). Heating rate 10 deg min^{-1}

Results and discussion

Table 1 presents the data obtained for all the investigated samples. The shapes of the DTA, TG and DTG curves of the samples stored over a saturated solution of NaCl were similar. As a typical example, Fig. 1 shows the curves obtained for sample H_4/I. It is seen that the fully hydrated samples begin to lose water at 40–50°, and most of it is given off below 170–200°. Such water is taken here as the water of crystallization. The water released at higher temperatures is assumed to be bonded in the form of OH groups, as the "water of constitution".

Table 1a

Sample	H_3/I	II	III	IV	V	H_4/I	II	III	IV	V
Conditions	NaCl	NaCl	NaCl	air	NaCl	NaCl	NaCl	N_2	air	NaCl
of preparation					+ air					+ air
Heating rate, deg/min	5	10	10	5	5	10	5	5	5	5
DTA peaks										
Endotherm I	—	—	—	—	—	55	57	—	—	—
Endotherm II	112	123	120	105	124	126	118	123	98	110
Endotherm III	134	150*	146*	135^d	137^d	150^d	132^d	—	126	130^d
Endotherm IV	153^d	167*	170	—	—	162^d	147^d	142^d	143^d	—
Endotherm V	—	—	—	—	—	360^d	333^d	350^d	350^d	331^d
Endotherm VI	435	427	434	436	433	450	450	450	450	452
Endotherm VII	784	789	780	$n.dt.$	$n.dt.$	$n.dt$	$n.dt.$	766		
Content of H_2O,										
molecules per										
Keggin unit:										
Total	31.42	27.05	27.42	20.62		36.19	34.96	11.77	15.40	10.31
Water of										
crystallization	29.96	$n.dt.$	26.01	19.37		34.25	32.28	9.92	14.01	8.39
Water of										
constitution	1.46	$n.dt.$	1.41	1.25		1.94	1.68	1.85	1.47	1.92
Average water										
of constitution			1.37 ± 0.09					1.77 ± 0.20		

NaCl = sample stored over a saturated solution of NaCl
air = sample stored in air
N_2 = sample kept in a current of dry nitrogen
^{d} = diffuse
* = DTG peak only
$^{n.dt.}$ = not determined
^{rw} = very weak

Table 1b

Sample	H_5/I	II	III	IV	V	H_6/I	II	III
Conditions of preparation	NaCl	air	NaCl	NaCl	NaCl + air	NaCl	NaCl	NaCl + air
Heating rate, deg/min	10	10	5	5	5	5	10	5
DTA peaks								
Endotherm I	49	40^{vw}	48	50	82^{vw}	48	52	—
Endotherm II	123	107	111	110	142	120	127	116
Endotherm III	146*	—	126*	126*	—	133^d	140^d	133^d
Endotherm IV	159^d	153^d	139^d	137^d	—	146^d	156*	—
Endotherm V	309^d	297^d	330^d	300^d	311^d	286^d	294^d	285^d
Endotherm VI	419	410	414	416	421	395	396	391
Endotherm VII	727	$n.dt.$	$n.dt$	$n.dt.$	$n.dt.$	716	$n.dt.$	$n.dt.$
Content of H_2O molecules per Keggin unit:								
Total	37.48	24.91	33.31	35.94	12.12	35.71		10.03
Water of crystallization	35.25	22.71	31.58	33.97	10.13	33.26		7.44
Water of constitution	2.23	2.20	1.73	1.97	1.99	2.45		2.59
Average water of constitution			2.02 ± 0.20				2.60 ± 0.15	

Depending on the initial water content of the samples, four to seven well-reproducible DTA peaks could be observed. With the exception of exothermic peak VI, all of them were endothermic. DTA peaks II–V were accompanied a loss in sample weight, which resulted in the appearance of analogous peaks in the DTG curves. In some cases, only DTG peaks were observed. The sensitivity of the apparatus was apparently not high enough to detect the parallel effects in the DTA curves. Such cases are appropriately indicated in Table 1.

The DTA peak at 55° for sample H_4/I and at similar temperatures in other cases corresponded to the partial or total fusion of the sample, or rather to its dissolution in its own water of crystallization, which was also observed visually in separate experiments. This peak was not observed for samples H_4–H_6, which partially lost water of crystallization when dried in air, as shown in Fig. 2 for sample H_6/III. Generally, the molybdovanadophosphoric acids did not exhibit this peak if their content of water of crystallization was below 14 H_2O molecules per Keggin unit. This peak was also absent for samples of molybdophosphoric acid ($x = 0$). In this case, visual observation indicated that in the fully hydrated sample the beginning of partial fusing occurred after heating above 105°. All the fused samples released
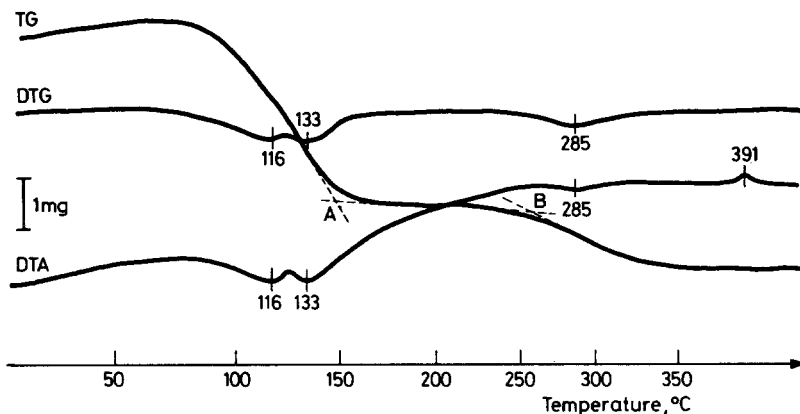
Fig. 2 Thermal curves of sample H_6/III ($H_{3.90}PMo_{11.10}V_{0.90}O_{40}$). Heating rate 5 deg min^{-1}

water, as shown by the TG and DTG curves in Fig. 1. Visual observation revealed boiling of the liquid at about 120°, which is why we interpreted the DTA peak at 126° in Fig. 1 as being connected with the evaporation of water from the saturated solutions of the HPA. This point was also accompanied by a break in the TG curve and a slowing-down of the further loss in weight.

The appearance of two subsequent peaks in the DTA and DTG curves, at 150 and 162° in Fig. 1, indicates that the departure of the remaining water of crystallization is not continuous and involves two lower hydrates. However, the two endothermic effects strongly overlap and it is difficult to give the exact compositions of the hydrates.

As may be seen from Table 1, the total amount of water of crystallization depends on the treatment of the sample. Under standard conditions, when samples were kept over a saturated solution of NaCl, the amount of water of crystallization was distinctly higher in the case of molybdovanadophosphoric acids (about 35 H_2O molecules per Keggin unit) than in the case of molybdophosphoric acid (26 to 30 H_2O molecules per Keggin unit). This may be due to the fact that in hydrated HPA protons released by acidic OH groups form hydrated complexes situated between anions formed by Keggin units [1]. The increasing number of OH groups in vanadium-containing molybdophosphoric acid may enhance the formation of such complexes and hence more water is bonded as water of crystallization.

When the samples are further heated after the water of crystallization has been lost, a plateau is observed in the TG curve; this is nearly horizontal in the case of slow heating (5 deg min^{-1}), but inclined in the case of more rapid heating (10 deg min^{-1}), as is to be seen in Fig. 1. The composition of the product remaining after the departure of the water of crystallization was determined from the point of

intersection of tangents to the portions of the TG curve adjacent to its bending. The decomposition of the anhydrous HPA started at temperatures which depend on the amount of vanadium introduced into the Keggin unit. It began at 414–425° and was characterized by flat weak DTA and DTG peaks in the case of preparation H_3, but for H_6 it began at about 250° and was accompanied by DTA and DTG peaks at about 290°. These data indicate clearly that the introduction of vanadium into the Keggin unit of 12-molybdophosphoric acid reduced the thermal stability of the HPA. The endothermic peak at 360° in Fig. 1 is followed by an exothermic one at 450°. The latter is not accompanied by a change in weight of the sample, which indicates some phase transformation. The departure of water molecules must necessarily be connected with the loss of some oxygen atoms from the Keggin unit. However, this need not be equivalent to the collapse of the structure of the HPA, as has been pointed out by Moffat [2]. Most probably, such a collapse is signalled by the exothermic peak. However, this peak may also be a result of spontaneous decomposition into the component oxides. In the case of sample H_3, the molybdophosphoric acid, which releases its water of constitution at a much higher temperature than that for the vanadium-containing HPA, the exothermic process occurs simultaneously with the dehydroxylation. In this case, instead of two DTA peaks, such as peaks V and VI in Fig. 1, only one exothermic peak is observed.
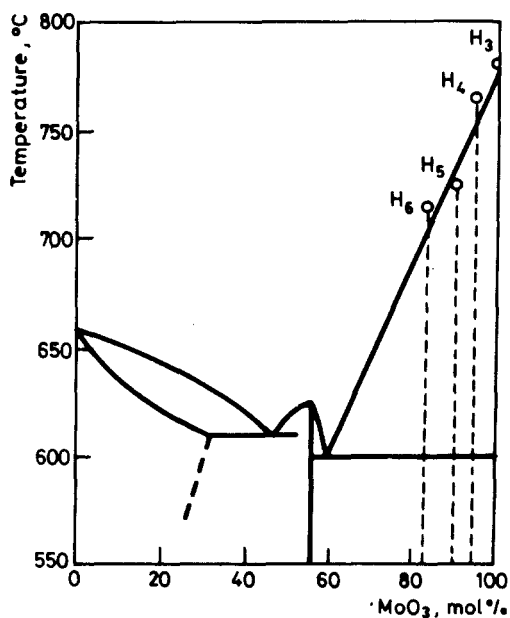

Fig. 3 V_2O_5–MoO_3 phase diagram. Points H_3, H_4, H_5 and H_6 show the fusion temperatures of the phosphorovanadomolybdenopolyacids

The number of acid OH groups calculated from the amount of water of constitution as determined thermogravimetrically, is lower than that expected; it is equal to 2.74, 3.54, 4.04 and 5.20, instead of 3.0 for H_3 and 3.90, 4.86 and 5.57 for samples H_4, H_5 and H_6, respectively, as calculated from the chemical compositions. This may be due to partial dehydroxylation before the departure of the residual water of crystallization. On the other hand, the above data are in better agreement with the amount of chemisorbed ammonia, the molar ratio NH_3/OH being 1.18, 0.962, 0.85 and 0.86 for samples H_3 to H_6, respectively. The values of 0.85 and 0.86 obtained for the least thermally stable samples H_5 and H_6, respectively, indicate that partial decomposition of the HPA occurred during the outgassing of the samples before the sorption of ammonia. The conditions of sorption of ammonia on such samples should therefore be studied in greater detail.

In a few cases, thermogravimetric analysis was extended to the temperature of fusion of the totally dehydrated product. It is interesting to observe that the temperatures of fusion given by the DTA peaks are in good accordance with the liquidus curve of the V_2O_5–MoO_3 phase diagram [10], as shown in Fig. 3.

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Zusammenfassung — An Molybdovanadophosphorsäuren der Formel $H_{(3+x)}Mo_{(12-x)}V_xO_{40} \cdot nH_2O$ ($x = 0, 1, 2, 3$) wurden DTA-, TG- und DTG-Untersuchungen durchgeführt. Die Proben mit dem größten Kristallwassergehalt ($n = 19$–34) schmelzen oberhalb 40 °C und liefern damit Lösungen von Heteropolysäuren mit einem Siedepunkt zwischen 110 und 130 °C. Der vollständige Verlust des Kristallwassers erfolgt unterhalb 170–200 °C. Die wasserfreien Säuren zersetzen sich (Dehydroxylierung) bei Temperaturen mit einem Durchschnittswert von 433 °C für $x = 0$ bis herab zu 293 °C für $x = 3$. Bei diesen vanadiumhaltigen Proben tritt für $x = 1, 2$ und 3 bei den Temperaturen 450, 430 und 390 °C ein exothermer Peak auf, der von keinem Gewichtsverlust begleitet wird und somit auf eine Strukturänderung des festen Zustandes hinweist. Bei $x = 0$ wird ein stärkerer exothermer Effekt von einem schwächeren endothermen überlagert und es existiert bei 435 °C nur ein exothermer Effekt.

Резюме — Проведены ДТА, ТГ и ДТГ исследования молибденванадофосфорных кислот общей формулы $H_{3+x}Mo_{12-x}V_xO_{40} \cdot nH_2O$, где $x = 0, 1, 2, 3$. Образцы с наибольшим содержанием кристаллизационной воды ($n = 19-34$) плавятся выше 40°, давая растворы гетерополикислот с температурами кипения 110–130°. Безводные кислоты разлагаются (дегидроксилирование) при среднем значении температур от 433° для $x = 0$ до 293° для $x = 3$. Для этих ванадийсодержащих образцов экзотермический пик, наблюдаемый, соответственно, при 340, 430 и 390° для $x = 1, 2, 3$, не сопровождается потерей веса, что указывает на фазовое превращение в твердом состоянии. При $x = 0$ более слабый эндотермический эффект дегидроксилирования перекрывается более сильным экзотермическим эффектом, вследствии чего он только и наблюдается при 435°.