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# THERMAL PROPERTIES OF BARIUM HEXAVANADATES

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## ABSTRACT

The thermal properties of $BaV_6O_{16} \cdot 5H_2O$ and $Ba(HV_6O_{16})_2 \cdot 7H_2O$ were studied by DTA, DTG and TG in the temperature interval 20–800°C. The dehydration of $BaV_6O_{16} \cdot 5H_2O$ is a continuous process, whereas the release of water from $Ba(HV_6O_{16})_2 \cdot 7H_2O$ proceeds in three steps. Both compounds are thermally unstable: they decompose with the formation of new compounds which all partially react together. As final products of thermal decomposition of both hexavanadates, mixtures containing $Ba(VO_3)_2$, $V_2O_5$ and $BaV_8O_{20.8}$ were identified.

## INTRODUCTION

The different types of polyvanadate hydrates can be classified, from the point of view of their thermal properties, into two groups:

(1) Polyvanadates in which even total dehydration does not cause a change in nature of the polymeric anion structure. For example, metavanadates containing chains formed by V–O polyhedra in their structures are known as crystallohydrates as well as being anhydrous compounds [1]. Their dehydration causes either a deformation of V–O polyhedra or a change in the coordination polyhedron of the vanadium atom, but the chain structure of the polyvanadate anion, typical for metavanadates, remains unchanged [2].

(2) Polyvanadates with structure stabilized by crystal water, the release of which is accompanied by structure decomposition and formation of new types of polyvanadates [3]. For example, decavanadates, containing voluminous $V_{10}O_{28}^{6-}$ ions as an isolated structural unit [4] in their structures exist only in the form of crystallohydrates.

Anhydrous polyvanadates with layer structure formed by V–O polyhedra are also known, $M^I_2V_6O_{16}$ ($M^I$ = K, Rb, Cs, Tl, $NH_4^+$) [5] and $M^I_3V_5O_{14}$ pentavanadates ($M^I$ = K, Rb, Tl) [6] but the structure of no polyvanadate crystallohydrate with layer structure is known so far. Based on the results obtained by indirect methods, hexavanadate hydrates can be regarded either as polyvanadates with layer structure or polyvanadates with isolated structural units. Therefore, it was of interest to find out the function of water in layer structures and, by studying its thermal properties, to obtain useful information about the structure of the polyvanadate anion [7–9]. This work is a contribution towards the solution of this problem.

## METHODS

$BaV_6O_{16} \cdot 5H_2O$ and $Ba(HV_6O_{16})_2 \cdot 7H_2O$ were prepared according to ref. 10 and identified by chemical analysis, IR spectroscopy and X-ray diffraction methods.

The thermal analysis was performed on a Q 1500 D derivatograph (MOM, Budapest). Conditions: air atmosphere, heating rate 10°C $min^{-1}$, sample mass 200 mg, Pt crucibles, $Al_2O_3$ as internal standard.

The IR spectra were measured in nujol mulls on a Perkin-Elmer 180 spectrophotometer. X-ray diffraction patterns were registered on a Philips PW 1050 diffractometer, using Cu$K\alpha$ radiation.

Vanadium(V) and vanadium(IV) were estimated by $FeSO_4$ ($c = 0.1$ mol $l^{-1}$) and $KMnO_4$ ($c = 0.01$ mol $l^{-1}$) titrations, respectively. Barium was estimated gravimetrically as $BaSO_4$.

## RESULTS AND DISCUSSION

To explain the endo- and exothermic peaks on the DTA curves, the heating of $Ba(HV_6O_{16})_2 \cdot 7H_2O$ was interrupted at 155, 270, 360, 430, 580, 630 and 800°C and that of $BaV_6O_{16} \cdot 5H_2O$ at 205, 300, 355, 455, 580 and 800°C (Fig. 1). The products were cooled to room temperature and their compositions were estimated by X-ray phase analysis and IR spectroscopy (Table 1).

The compounds studied differ in the nature of their mass loss: in $BaV_6O_{16} \cdot 5H_2O$ it is a one-step process ending at 300°C, while in $Ba(HV_6O_{16}) \cdot 7H_2O$ it proceeds in three steps. The individual steps of mass loss in $Ba(HV_6O_{16})_2 \cdot 7H_2O$ do not correspond to integer values of water molecules, since the individual processes overlap. However, it is evident that the third step corresponds to the release of the last traces of water from OH groups (approx. 0.5%, total 1.3%) which stabilizes the parent structure. The third step ends just below the maximum temperature of the exothermic peak on the DTA curve (360°C, Fig. 1). The mass loss found is greater than that calculated for total dehydration in both compounds (for $Ba(HV_6O_{16})_2 \cdot 7H_2O$: calc.: 10.38%, found: 10.62%; for $BaV_6O_{16} \cdot 5H_2O$: calcd.: 11.42%, found: 12.46%). From this fact, as well as from the composition of products obtained at 430 and 455°C (Table 1), it follows that the water release is accompanied by elimination of oxygen in both compounds. The more distinct difference between the calculated and found values of mass loss in

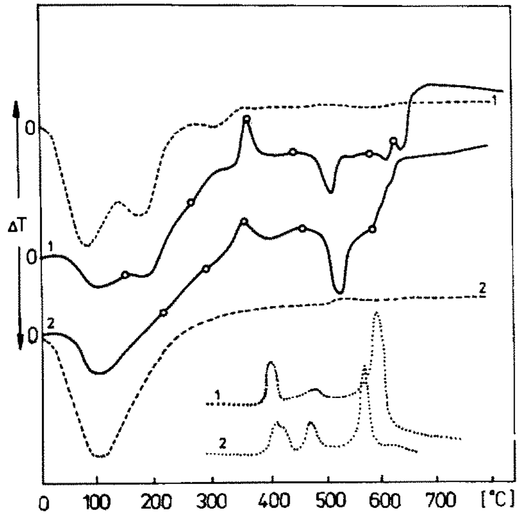

Fig. 1. Thermoanalytical curves of $Ba(HV_6O_{16})_2 \cdot 7H_2O$ (1) and $BaV_6O_{16} \cdot 5H_2O$ (2). (———) DTA, (- - - - -) DTG, (· · · · · ·) DTA of cooling, (○) heating interruption.

$BaV_6O_{16} \cdot 5H_2O$ is caused by the presence of a greater proportion of vanadium–oxygen bronzes in the products discussed.

The X-ray diffraction patterns of products obtained by heating interrupted at temperatures corresponding to exothermic peaks show that new compounds with incompletely built structures are formed. However, their IR spectra are already similar to those of products obtained at 430 and 455°C which already exhibit good quality diffraction patterns. As follows from Table 1, these products each contain the compounds $BaV_8O_{20.8}$ and $BaV_6O_{16}$.

Anhydrous hexavanadates with a bivalent cation have not been mentioned in the literature so far. Compounds with formula $M^I_2V_6O_{16}$ are formed only

TABLE 1

Composition of products of thermal decomposition

| Temp. (°C) | $Ba(HV_6O_{16})_2 \cdot 7H_2O$ | Temp. (°C) | $BaV_6O_{16} \cdot 5H_2O$ |
|---|---|---|---|
| 155 | $Ba(HV_6O_{16})_2 \cdot xH_2O$ | 205 | $BaV_6O_{16} \cdot xH_2O + Z$ [b] |
| 270 | $Ba(HV_6O_{16})_2$ | 300 | $BaV_6O_{16} + Z$ [b] |
| 430 | $V_2O_5$, $BaV_6O_{16}$, $BaV_8O_{20.8}$ | 455 | $BaV_6O_{16}$, $BaV_{12}O_{30}$, $BaV_8O_{20.8}$, $Ba_2V_6O_{16}$ |
| 580 | $Ba(VO_3)_2$, $V_2O_5$, $BaV_8O_{20.8}$ [a] | 580 | $Ba(VO_3)_2$, $V_2O_5$, $BaV_8O_{20.8}$ [a] |
| 630<br>800 | $Ba(VO_3)_2$, $V_2O_5$, $BaV_8O_{20.8}$, $Ba_2V_6O_{16}$ [a] | 800 | $Ba(VO_3)_2$, $V_2O_5$, $BaV_8O_{20.8}$ |

[a] Traces.

[b] Z = traces of unidentified admixture.

TABLE 2

Interplanar distances (nm) in the products of thermal decomposition of the compounds studied (diffraction patterns were recorded at Comenius University)

| $Ba(HV_6O_{16})_2 \cdot 7H_2O$ | | | | | | $BaV_6O_{16} \cdot 5H_2O$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 430°C | | 580°C | | 800°C | | 455°C | | 580°C | | 800°C | |
| $d_{hkl}/I_{rel}$ | | $d_{hkl}/I_{rel}$ | | $d_{hkl}/I_{rel}$ | | $d_{hkl}/I_{rel}$ | | $d_{hkl}/I_{rel}$ | | $d_{hkl}/I_{rel}$ | |
| 0.936/7 | H | 0.706/12 | M | 0.783/5 | Ω | 0.938/6 | H | 0.708/8 | M | 0.708/2 | M |
| 0.723/5 | Φ | 0.575/32 | O | 0.727/9 | Φ | 0.787/3 | Ω | 0.577/12 | O | 0.578/4 | O |
| 0.571/12 | O | 0.475/2 | Φ | 0.704/16 | M | 0.750/8 | B | 0.472/2 | Φ | 0.472/4 | Φ |
| 0.478/7 | Φ | 0.438/95 | O | 0.574/24 | O | 0.721/3 | Φ | 0.439/35 | O | 0.437/30 | O |
| 0.437/30 | O | 0.409/27 | O | 0.493/4 | M | 0.671/8 | | 0.409/15 | O | 0.408/6 | O |
| 0.409/10 | O | 0.375/8 | M | 0.475/11 | Φ | 0.590/4 | H | 0.396/4 | M | 0.394/4 | M |
| 0.346/3 | O | 0.346/39 | MO | 0.437/100 | O | 0.520/5 | H | 0.375/12 | M | 0.375/6 | M |
| 0.339/80 | OΦ | 0.341/100 | OM | 0.408/90 | O | 0.477/10 | BΦ | 0.346/27 | MO | 0.343/7 | MO |
| 0.316/4 | Φ | 0.322/40 | M | 0.394/5 | MΩ | 0.417/8 | Ω | 0.341/72 | OM | 0.339/32 | OM |
| 0.2939/7 | Φ | 0.2931/12 | MΦ | 0.373/9 | M | 0.394/3 | BΩ | 0.322/38 | M | 0.320/25 | M |
| 0.2880/35 | O | 0.2890/75 | OM | 0.358/4 | Ω | 0.365/4 | B | 0.2940/15 | MΦ | 0.314/6 | Φ |
| 0.2755/11 | O | 0.2760/37 | MO | 0.344/38 | MO | 0.346/7 | B | 0.2880/43 | OM | 0.305/4 | Φ |
| 0.2690/6 | O | 0.2690/10 | MO | 0.340/95 | OMΦ | 0.338/64 | HΦ | 0.2770/22 | MO | 0.2921/10 | MΦ |
| 0.2610/15 | O | 0.2610/30 | OM | 0.322/39 | MΩ | 0.322/6 | BΩ | 0.2681/4 | MO | 0.2882/20 | OM |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.2170/5 | OΦ | 0.2417/14 | MO | 0.315/8 | ΦΩ | 0.316/17 | BΩΦ | 0.2622/16 | OM | 0.2760/6 | MO |
| 0.1985/5 | O | 0.2300/4 | M | 0.307/8 | ΩΦ | 0.300/15 | ΦΩ | 0.2418/14 | MO | 0.2690/4 | MO |
| 0.1910/10 | O | 0.2254/20 | M | 0.2930/15 | MΦ | 0.2960/23 | BHΦΩ | 0.2348/6 | M | 0.2611/6 | OM |
| 0.1855/7 | O | 0.2185/55 | MO | 0.2885/90 | OM | 0.2860/32 | H | 0.2251/21 | M | 0.2410/6 | MO |
| 0.1791/4 | Φ | 0.2161/17 | MO | 0.2760/37 | MOΩ | 0.2710/10 | BΩ | 0.2196/13 | MO | 0.2331/3 | M |
| 0.1770/9 | OH | 0.2120/5 | M | 0.2690/9 | MO | 0.2530/5 | ΦΩ | 0.2166/17 | MO | 0.2244/12 | M |
| 0.1753/2 | O | 0.2034/3 | M | 0.2610/21 | OM | 0.2368/3 | BΩ | 0.2118/8 | M | 0.2180/15 | MO |
| 0.1642/5 | O | 0.1993/10 | OM | 0.2490/3 | M | 0.2260/8 | BH | 0.2024/3 | M | 0.2150/8 | MO |
| | | 0.1918/20 | O | 0.2410/17 | MO | 0.2139/4 | Φ | 0.1998/6 | OM | 0.2110/3 | M |
| | | 0.1869/17 | MO | 0.2300/5 | M | 0.2090/18 | BHΩ | 0.1974/5 | M | 0.1987/3 | OM |
| | | 0.1781/20 | O | 0.2250/20 | M | 0.2040/5 | BΩ | 0.1920/13 | O | 0.1908/3 | O |
| | | 0.1759/14 | OM | 0.2186/65 | MO | 0.1935/3 | B | 0.1879/6 | M | 0.1890/4 | OM |
| | | 0.1701/8 | M | 0.2150/35 | MO | 0.1868/3 | B | 0.1869/14 | MO | 0.1863/7 | MO |
| | | 0.1652/7 | O | 0.2117/7 | M | 0.1831/7 | B | 0.1824/4 | M | 0.1783/4 | MO |
| | | 0.1610/3 | M | 0.2036/4 | M | 0.1797/28 | BΦ | 0.1784/8 | MO | 0.1743/4 | OM |
| | | 0.1568/7 | OM | 0.1993/8 | OM | 0.1583/6 | | 0.1759/9 | OM | 0.1698/4 | M |
| | | | | 0.1922/12 | O | | | 0.1714/4 | M | | |
| | | | | 0.1903/25 | OM | | | | | | |
| | | | | 0.1870/21 | OM | | | | | | |
| | | | | 0.1796/5 | Φ | | | | | | |
| | | | | 0.1780/17 | OM | | | | | | |
| | | | | 0.1760/12 | MO | | | | | | |

O, $V_2O_5$; B, $BaV_{12}O_{30}$; Φ, $BaV_8O_{20.8}$; Ω, $Ba_2V_6O_{16}$ [13]; M, $Ba(VO_3)_2$; H, $BaV_6O_{16} \cdot xH_2O$.

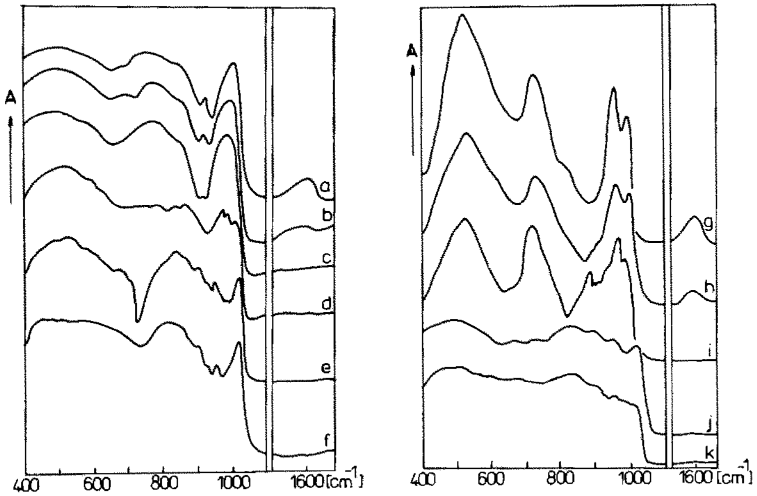

Fig. 2. IR spectra of $Ba(HV_6O_{16})_2 \cdot 7H_2O$ (a), $BaV_6O_{16} \cdot 5H_2O$ (g) and products of their thermal decomposition at various temperatures: (b) 155, (c) 270, (d) 360–430, (e) 580, (f) 630–800, (h) 205, (i) 355–455, (j) 580, (k) 800°C.

with large univalent cations. Their structures are formed by $VO_5$ polyhedra being linked in layers with the cations placed between the layers [5]. $BaV_6O_{16}$ was identified in the mixture on the basis of the IR absorption bands characteristic of hexavanadates (Fig. 2) and the most intense diffractions which are, in comparison with $BaV_6O_{16} \cdot 5H_2O$, slightly shifted. Pure anhydrous $BaV_6O_{16}$ cannot be prepared by dehydration of $BaV_6O_{16} \cdot 5H_2O$ despite the fact that the ionic radii of $Ba^{2+}$ and $K^+$ are similar. The product obtained by heating interrupted at 205°C still contains water but its IR spectrum already exhibits a new absorption band of vanadium–oxygen bronze (Fig. 2). The lower thermal stability of $BaV_6O_{16}$ is evidently caused by a less advantageous Ba : V molar ratio (1 : 6) compared with K : V = 1 : 3 in $K_2V_6O_{16}$. It was found that in alkali hexavanadates of composition $M^I_2V_6O_{16}$ ($M^I$ = K, Rb, Cs), the greater the ionic radius the greater the thermal stability. $K_2V_6O_{16}$ completely decomposes within the temperature interval 415–560°C, whereas $Rb_2V_6O_{16}$ and $Cs_2V_6O_{16}$ hexavanadates are the essential components in the mixture even at 800°C [11]. Further, it cannot be ignored that $BaV_6O_{16}$, similar to $NaV_3O_8$, contains, in addition to vanadium(V), a small amount of vanadium(IV). However, we cannot answer this question on the basis of experimentally detected vanadium(IV), since the products obtained at temperatures higher than 200°C also contain vanadium–oxygen bronzes.

These facts indicate that the endothermic peaks connected with mass loss and observed on the DTA curves of both compounds are a result of a superposition of dehydration and redox reactions accompanied by the release of oxygen and partial reduction of vanadium(V) to vanadium(IV). The exothermic peaks with maxima at 355 and 360°C correspond either to the total decomposition of parent structure in $Ba(HV_6O_{16})_2 \cdot 7H_2O$ or to the partial decomposition of $BaV_6O_{16} \cdot 5H_2O$ and formation of new compounds which gradually crystallize at higher temperatures. Formation of the identified products can be described by following equations

$$2Ba(HV_6O_{16})_2 \cdot 7H_2O = BaV_6O_{16} + 5V_2O_5 + BaV_8O_{20.8} + 16H_2O + 0.1O_2$$

$$8BaV_6O_{16} \cdot 5H_2O = 3BaV_8O_{20.8} + BaV_{12}O_{30} + 2Ba_2V_6O_{16} + 40H_2O + 2O_2$$

In the temperature interval 500–580°C, both compounds oxidatively melt and thermally unstable vanadium–oxygen bronzes as well as $BaV_6O_{16}$ decompose to $V_2O_5$ and $Ba(VO_3)_2$. As follows from Table 1, both mixtures have the same qualitative composition at 580°C.

$BaV_8O_{20.8}$ oxidatively melts within the temperature interval 540–580°C. According to refs. 12 and 13, $BaV_8O_{20.8}$ dissociates at increased temperatures, however, the melt and solid have the same composition. Therefore, on crystallization from the melt $BaV_8O_{20.8}$ is formed again without fixation of oxygen. The presence of $BaV_8O_{20.8}$ in products formed by crystallization from the melt can be explained in this way. (In the mixture obtained at 580°C only a small amount was formed; in the X-ray diffraction pattern only the most intense diffractions were observed; see Table 2.)

Complicated thermochemical reactions between components of the mixture under formation of $BaV_8O_{20.8}$ proceed in the temperature interval 580–800°C. From the products of thermal decomposition of $Ba(HV_6O_{16})_2$, the formation of $Ba_2V_6O_{16}$ takes place.

The DTA curves on cooling exhibit three exothermic peaks: the first one, with maxima at 600 and 565°C, was assigned to crystallization of $BaV_8O_{20.8}$; the second peak, with maxima at 470 and 450°C, was attributed to the modified transformation of $Ba(VO_3)_2$ (which was observed on the thermoanalytical curves of pure $Ba(VO_3)_2 \cdot H_2O$, studied in an attempt to explain the thermal behaviour of hexavanadates); and third peak with maxima at 402 and 410°C, was assigned to the crystallization of the eutectic $Ba(VO_3)_2$–$V_2O_5$ mixture. According to ref. 13, the crystallization of $V_2O_5$ and the eutectic $M^{II}(VO_3)_2$–$V_2O_5$ mixture is characterized by strong undercooling, in agreement with our results.

From the study of thermal properties of $Ba(HV_6O_{16})_2 \cdot 7H_2O$ and $BaV_6O_{16} \cdot 5H_2O$ it follows that the structure of hydrogen hexavanadate is stabilized by part of the water bound via OH groups, whereas hexavanadate partially decomposes on the release of the last crystal water molecules. The composition of products of thermal decomposition depends on the thermal stability of individual polyvanadates and vanadium–oxygen bronzes and on the stoichiometry of the parent compounds.

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