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THERMAL REACTIVITY OF DECAVANADATES

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A study of the thermal decomposition of crystal hydrates of decavanadates confirmed the stabilizing role of the crystal water in their structures. The original structure is destroyed after dehydration, and lower condensed vanadates and oxides of vanadium are formed. The course of thermal decomposition of the decavanadates depends on the bonding properties of the concrete elements present. The ability of a given element to form a certain type of vanadate, the thermal stability and the stoichiometry of the original compound are the main factors influencing the composition of the products of thermal decomposition of the vanadates studied.

It is known that virtually all decavanadates synthetized up to the present time have 4–28 moles of water per mole of decavanadate in their structures. Decavanadates with organic cations are an exception [1, 2]. The importance of the crystal water in decavanadates follows from the structural individuality of this type of polyvanadates. The structures contain a bulky anion $V_{10}O_{28}^{6-}$, composed of ten VO_6 octahedra linked to each other by their edges. Cations are usually coordinated by molecules of water [3–5]. These molecules of water enlarge the volume over which the cations in the structure function. Moreover, they strengthen the bonding interactions between the structural units by the creation of hydrogen-bonds to the oxygens of the $V_{10}O_{28}^{6-}$ anion. With regard to this fact, it is inevitable to suppose that the dehydration of decavanadates will cause destabilization of the original structure, leading eventually to its decomposition.

At present, a relatively large number of decavanadates are known. These compounds contain cations with different bonding properties and their formulae display different molar ratios metal: $V_{10}O_{28}^{6-}$ (6 : 1, 5 : 1, 4 : 1, 3 : 1 and 2 : 1). We assumed that the given factors could have a very significant influence on the thermal reactivity of decavanadates, and we therefore considered it necessary to study a sufficient number of compounds. Decavanadates of the composition $M_6^IV_{10}O_{28} \cdot xH_2O$ (M^I = Li, Na, K, Rb, Cs, Tl), $M_3^{II}V_{10}O_{28} \cdot xH_2O$ (M^{II} = Mg, Ca, Sr, Ba, Zn, Cd), $K_2Cd_2V_{10}O_{28} \cdot 14\ H_2O$, $Cs_2Zn_2V_{10}O_{28} \cdot 14\ H_2O$, $(NH_4)_4CdV_{10}O_{28} \cdot 14\ H_2O$, $Tl_4Na_2V_{10}O_{28} \cdot 10\ H_2O$, $Tl_4CoV_{10}O_{28} \cdot 10\ H_2O$, $Y_2V_{10}O_{28}\ .\ 24\ H_2O$ and $La_2V_{10}O_{28} \cdot 24-25\ H_2O$ were investigated.

The procedures used included continuous differential thermal analysis, interrupted DTA and isothermal drying over several dryers and at certain temperatures. The products were studied by means of IR and EPR spectroscopy and X-ray phase analysis.

From the results of thermal analysis of the investigated compounds it follows that complex physico-chemical reactions occur under the influence of heat (Table 1). It is possible to state that, as a rule, two or more physico-chemical reactions occur in the majority of the temperature intervals given in the Table. Endothermic processes are connected with dehydration of the compounds, with the structural changes corresponding to this, and with the partial reduction of vanadium(V) to vanadium(IV). Exothermic processes correspond to crystallization of the products of the destructive reactions and usually to the redox reactions too. It is also necessary to consider in some cases the possibility of mutual reactions between the products of decomposition of the compounds investigated at higher temperatures.

The described research has unambiguously confirmed the stabilizing role of crystal water in the structures of decavanadates. However, it is impossible to determine the exact number of molecules of water necessary to stabilize the structure of the arbitrary decavanadates, because this amount depends on the size and bonding properties of a given cation. Following the loss of this required amount of water, the structure of the decavanadate is destroyed.

However, the bonding properties do not only determine the minimum number of molecules of crystal water which must be present in solid decavanadates, but also decisively influence some other thermal actions arising as a consequence of dehydration of the given compounds. These are the decomposition reactions which

Table 1

Temperature intervals in °C in which thermal effects are observed

Compound	Endothermic effects	Exothermic effects
$K_6V_{10}O_{28} \cdot 10\ H_2O$	50 – 100, 100 – 280	—
$Rb_6V_{10}O_{28} \cdot 8-9\ H_2O$	45 – 115, 115 – 145, 145 – 175, 175 – 205	—
$Cs_6V_{10}O_{28} \cdot 9\ H_2O$	55 – 140, 140 – 190	—
$Tl_6V_{10}O_{28} \cdot 4\ H_2O$	75 – 140, 140 – 175	175 – 240
$Li_6V_{10}O_{28} \cdot 16\ H_2O$	90 – 260	260 – 365
$Na_6V_{10}O_{28} \cdot 10\ H_2O$	45 – 115, 115 – 160, 160 – 290	290 – 300
$Mg_3V_{10}O_{28} \cdot 18\ H_2O$	40 – 140, 140 – 265	340 – 400
$Ca_3V_{10}O_{28} \cdot 16\ H_2O$	75 – 125, 125 – 245	280 – 330, 380 – 420, 420 – 460
$Sr_3V_{10}O_{28} \cdot 24\ H_2O$	40 – 190, 190 – 280	315 – 365, 365 – 385
$Ba_3V_{10}O_{28} \cdot 19\ H_2O$	30 – 80, 80 – 180, 180 – 220	—
$Zn_3V_{10}O_{28} \cdot 18\ H_2O$	50 – 110, 110 – 240	260 – 330
$Cd_3V_{10}O_{28} \cdot 16\ H_2O$	75 – 190, 190 – 240	240 – 280
$K_2Cd_2V_{10}O_{28} \cdot 14\ H_2O$	50 – 80, 80 – 115, 115 – 180, 180 – 230	240 – 265
$Cs_2Zn_2V_{10}O_{28} \cdot 14\ H_2O$	60 – 230	—
$(NH_4)_4CdV_{10}O_{28} \cdot 14\ H_2O$	50 – 155, 155 – 275, 275 – 340	355 – 440, 440 – 485
$Y_2V_{10}O_{28} \cdot 24\ H_2O$	50 – 170, 170 – 250, 250 – 300	365 – 410
$La_2V_{10}O_{28} \cdot 24-25\ H_2O$	80 – 250	300 – 400, 400 – 480

result in the formation of vanadates with a smaller molar mass than in the original decavanadates. As regards the manner of dehydration and decomposition of the decavanadates, the investigated compounds can be divided into two groups. In the case of decavanadates of the first group (Table 2, I) crystallization of the decomposition products occurs even in the course of the release of the last molecules of water. In the second group of decavanadates (Table 2, II) the noncrystalline anhydrous intermediate arises primarily and the other vanadates arise successively from its decomposition at higher temperatures.

The fact deserves attention that in most cases the presence of vanadium(IV) was found in the course of the thermal reactions of the compounds studied. This fact is connected with the formation of various vanadium oxides and vanadium bronzes. The presence of these compounds in the decomposition products depends on their thermal stability and also on the possibility of attaining the required degree of reduction of vanadium under the given reaction conditions. Vanadium bronze is usually present in the product in small amount, as an admixture.

The principal components of the decomposition products are: vanadates of lower condensation, and vanadium oxides.

Table 2

Products of thermal decomposition of decavanadates

	Compound	Final products	T_1, °C	T_2, °C	Refs.
I	$K_6V_{10}O_{28} \cdot 10\ H_2O$	$K_3V_5O_{14}$	180	180	6, 7, 16
	$Rb_6V_{10}O_{28} \cdot 8-9\ H_2O$	$Rb_3V_5O_{14}$	150	150	6, 16
	$Cs_6V_{10}O_{28} \cdot 9\ H_2O$	$Cs_2V_4O_{11} + CsVO_3$	130	130	6
	$Tl_6V_{10}O_{28} \cdot 4\ H_2O$	$Tl_3V_5O_{14}$	200	200	7, 8, 16
	$Li_6V_{10}O_{28} \cdot 16\ H_2O$	$Li_2V_5O_{13.3} + LiVO_3$	300	200	6
	$Na_6V_{10}O_{28} \cdot 10\ H_2O$	$NaVO_3 + NaV_3O_8$	250	180	6, 9
	$Mg_3V_{10}O_{28} \cdot 18\ H_2O$	$Mg(VO_3)_2 + V_2O_5$	330	230	10
	$Ca_3V_{10}O_{28} \cdot 16\ H_2O$	$Ca(VO_3)_2 + V_2O_5$	400	280	11
	$Sr_3V_{10}O_{28} \cdot 24\ H_2O$	$Sr(VO_3)_2 + V_2O_5$	420	200	11
	$Ba_3V_{10}O_{28} \cdot 19\ H_2O$	$Ba(VO_3)_2 + V_2O_5$	420	220	11, 16
	$Zn_3V_{10}O_{28} \cdot 18\ H_2O$	$Zn(VO_3)_2 + V_2O_5$	270	200	9
	$(NH_4)_4CdV_{10}O_{28} \cdot 14\ H_2O$	$Cd(VO_3)_2 + V_2O_5$	240	350	13
II	$Cd_3V_{10}O_{28} \cdot 16\ H_2O$	$Cd(VO_3)_2 + V_2O_5$	250	200	10
	$K_2Cd_2V_{10}O_{28} \cdot 14\ H_2O$	$Cd(VO_3)_2 + K_2V_6O_{16}$	330	220	7
	$Cs_2Zn_2V_{10}O_{28} \cdot 14\ H_2O$	$Zn(VO_3)_2 + Cs_2V_6O_{16}$	310	220	12
	$Tl_4Na_2V_{10}O_{28} \cdot 10\ H_2O$	$Tl_3V_5O_{14}$ + Na–V bronze	—	—	16
	$Tl_4CoV_{10}O_{28} \cdot 10\ H_2O$	$Tl_3V_5O_{14} + Co(VO_3)_2$	—	—	16
	$Y_2V_{10}O_{28} \cdot 24\ H_2O$	$YVO_4 + V_2O_5$	400	360	14
	$La_2V_{10}O_{28} \cdot 24-25\ H_2O$	$LaVO_4 + V_2O_5 + V_4O_7$	300	150	15

T_1 = lowest temperature of identification of products.
T_2 = temperature of dehydration.

With respect to the structures of the anions of the vanadates in question, these can be divided into three groups:

1. layer structures (hexa- and pentavanadates),
2. chain structures (metavanadates),
3. "isolated" VO_4 tetrahedra (ortovanadates).

Evaluation of the research into the thermal reactivities of the decavanadates enables us to pin-point the factors which influence the composition of the products of the thermal reactions studied. These factors are: 1. the ability of a given cation to form a certain type of vanadate, 2. the thermal stability of the vanadate under consideration, 3. the stoichiometry of the original salt.

All given factors are of equal importance and their mutual relations must be considered in the case of a concrete decavanadate. This is demonstrated in Table 3,

Table 3

Relation between the composition of the products of decomposition and the oxidation state of the element M

Oxidation state of the element M	Product of thermal decomposition of decavanadate
I	$M_3V_5O_{14}$, $M_2V_6O_{16}$, MVO_3, $Cs_2V_4O_{11}$
II	$M(VO_3)_2$, V_2O_5
III	MVO_4, V_2O_5

which gives generalized results of the present research. It follows from the table that the degree of condensation of the vanadates formed by decomposition of the original structure decreases with increasing oxidation state of the element present in the original decavanadate. Considering the structural aspects of the possible products of decomposition of the decavanadates given in the Table, we can claim that metals with oxidation state II and III are not able to form anhydrous vanadates for which a layer structure of the anions is characteristic; metals with oxidation state III are not able to form even anhydrous vanadates with an anion chain structure.

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Résumé — L'étude de la décomposition thermique des décavanadates hydratés et cristallisés a confirmé l'action stabilisatrice de l'eau de cristallisation dans leur structure. La structure originale est détruite après déshydratation; des vanadates moins condensés, et les oxydes de vanadium respectifs se forment. L'allure de la décomposition thermique des décavanadates dépend des propriétés des liaisons d'un élément donné présent dans la structure d'un décavanadate. L'aptitude d'un élément donné à former un certain type de vanadates, la stabilité thermique et la stoechiométrie du composé original sont les facteurs principaux qui influencent la composition des produits de la décomposition thermique des vanadates étudiés.

Zusammenfassung — Die Untersuchungen der thermischen Zersetzung der Kristallhydrate von Dekavanadaten bestätigte die Stabilisationswirksamkeit des Kristallwassers in ihrer Struktur. Die Originalstruktur wird nach der Dehydratisierung zerstört und weniger kondensierte Vanadate, bzw. Vanadiumoxide werden gebildet. Der Verlauf der thermischen Zersetzung der Dekavanadate hängt von den Bindungseigenschaften eines in der Struktur eines Dekavanadates vorhandenen konkreten Elements ab. Die Fähigkeit eines gegebenen Elements einen gewissen Typ von Vanadaten zu bilden, seine thermische Stabilität und die Stöchiometrie der Originalverbindung sind die Hauptfaktoren, welche die Zusammensetzung der Produkte der thermischen Zersetzung der untersuchten Vanadate beeinflussen.

Резюме — Изучение термического разложения кристаллогидратов декаванадатов подтвердило стабилизирующее действие кристаллизационной воды, входящей в их структуру. Первоначальная структура после дегидратации нарушается и образуются, соответственно, более низкоконденсированные ванадаты и окислы ванадия. Ход термического разложения декаванадатов зависит от связывающих свойств конкретного элемента, присутствующего в структуре декаванадата. Установлено, что способность данного элемента образовывать определенный тип ванадатов, их термическая стабильность и стехиометрия первоначального соединения являются главными факторами, затрагивающими состав продуктов термического разложения ванадатов.