

STUDY OF THERMAL PROPERTIES OF POTASSIUM μ -HYDROXO-BIS(OXO-DIPEROXOVANADATE) (V)

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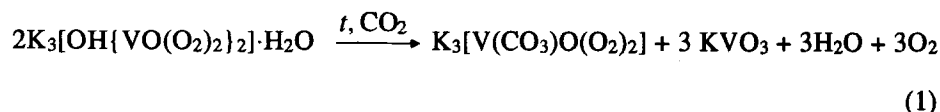
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The thermal decomposition of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ was studied under dynamic conditions up to 350°C and also isothermally at 150 \pm 3°C in self-generated atmosphere. $K_4[V_2O_6(O_2)]$ is formed as the reaction intermediate. The final products of thermal decomposition of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ are KVO_3 and $K_4V_2O_7$.

Keywords: potassium μ -hydroxo-bis(oxo-diperoxovanadate(V)), thermal decomposition

Introduction

The thermal decomposition of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ was studied under isothermal conditions at 100°C in air atmosphere [1]. The stoichiometry of the thermal decomposition process in the presence of CO_2 from air can be described by the Eq. (1)



The resulting vanadium compounds, $K_3[V(CO_3)O(O_2)_2]$ and KVO_3 , are products of reactions in which the coordinatively unsaturated intermediates are stabilized and formed after a partial oxygen release from the coordinated peroxy groups.

We report here the study of thermal decomposition of the starting compound under conditions not allowing to react with CO_2 from air.

Experimental

$K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ was prepared according to [1]. Vanadium(V) was determined by titration with iron(II) sulphate after the sample heated for a short time to release the peroxy oxygen. The peroxide content was estimated by potentiometric titration with potassium permanganate. Potassium was determined by flame photometry (Flapho 4, by Zeiss, Jena). X-ray powder diffraction patterns were recorded using a Philips diffractometer (PW 1050) and $CuK\alpha$ radiation. The IR spectra in Nujol mulls were measured using a Specord M 80 spectrophotometer (Zeiss, Jena). The DTA and TG curves were measured on a Derivatograph Q-1500 D (system: F. Paulik, J. Paulik, L. Erdey) (MOM Budapest). 600 mg of the powdered substance was heated. Heating rate was $5\text{ deg}\cdot\text{min}^{-1}$ in a static air atmosphere up to 188° or 350°C . The isothermal decomposition of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ at $150^\circ\pm 3^\circ\text{C}$ proceeded 21 days in a self-generated atmosphere in a glass vessel closed by Bunsen valve. To avoid changes in the self-generated atmosphere by opening the vessel that could thus initiate further reaction of the solid decomposition products, the samples were parallel decomposed in several vessels and the decomposition was interrupted successively on the basis of the weight loss monitored.

The course of thermal reactions was followed by means of weight loss, infrared spectroscopy, chemical analyses and the X-ray powder patterns of the solid

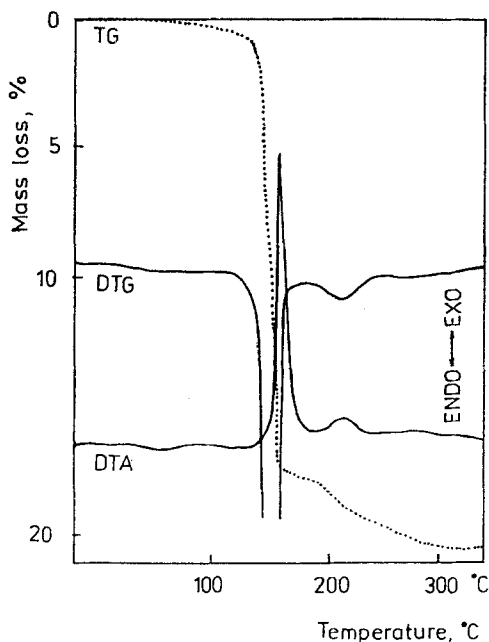


Fig. 1 Thermoanalytical curves of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$

decomposition products after cooling to room temperature in a desiccator above KOH.

Results and discussion

The DTA and TG curves of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ are shown in Fig. 1. The thermal decomposition is a multistep process. The first step on the TG curve ($\Delta m = 19.1\%$) which is accompanied by a strong exothermic effect with maximum at $170^\circ C$ corresponds to the release of water and to a partial release of oxygen from the coordinated peroxy groups and it is in agreement with the value $\Delta m = 19.1\%$, calculated from Eq. (2).

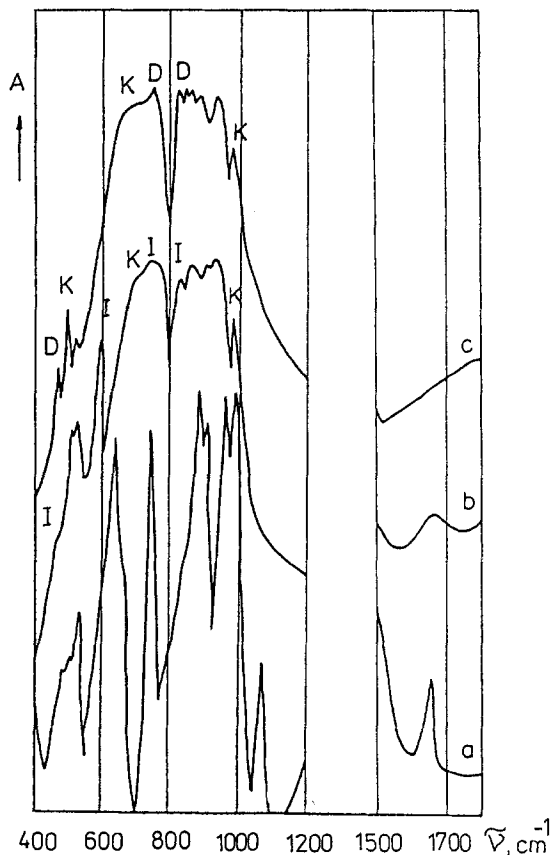


Fig. 2 IR spectrum of $K_3[OH\{VO(O_2)_2\}_2]\cdot H_2O$ (a), of the product of TA up to 188° (b) and $350^\circ C$ (c). Designation of characteristic absorption bands of KVO_3 - K, $K_4[V_2O_6(O_2)]\cdot 3H_2O$ - I and $K_4V_2O_7$ - D

Table 1 X-ray powder patterns of the product of TA up to 350°C (P₃₅₀), up to 188°C (P₁₈₈), KVO₃, K₄[V₂O₆(O₂)]·3H₂O and K₄V₂O₇

P ₃₅₀		P ₁₈₈		K ₄ [V ₂ O ₆ (O ₂)]·3H ₂ O*		KVO ₃ [3]		K ₄ V ₂ O ₇ ^a	
d / nm	I	d / nm	I	d / nm	I	d / nm	I	d / nm	I
0.514	11	0.511	8	0.491	12	0.512	11	0.489	11
		0.493	10					0.486	11
		0.468	9	0.464	11			0.461	8
		0.407	13	0.407	10			0.404	12
0.389	10	0.390	8			0.390	8		
0.372	14	0.370	8			0.371	6		
		0.359	6	0.360	5	0.359	5		
		0.345	6	0.344	5				
0.337	18							0.337	17
		0.317	25	0.312	33			0.324	9
0.310	100	0.312	52			0.311	100	0.312	25
		0.307	100	0.307	100				
0.305	59							0.305	100
		0.290	53	0.289	65			0.291	10
0.288	52							0.286	74
0.283	52	0.282	18					0.279	11
0.270	19			0.273	15			0.268	13
0.260	25	0.257	13			0.260	20	0.259	7
0.243	19	0.242	10			0.243	11	0.244	7
0.233	16	0.234	19	0.233	21	0.230	9	0.232	20
229	19							0.221	6
0.202	9	0.203	15	0.204	22			0.202	20
		0.195	7			0.195	6	0.192	5

*Our results

Table 2 Absorption bands in the IR spectra of some decomposition products of $K_3[OH(VO(O_2)_2)_2] \cdot H_2O$ (1200–400 cm^{-1})

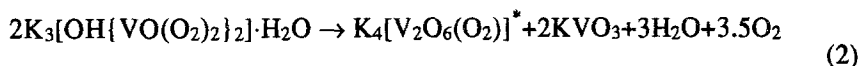
P_1^a	P_2^b	P_F^c	Compounds ^d
1050 vw			S
970 s	970 s	965 s	S, K
	930 vs	930 vs	K, D
920 s, b			I, K, D
870 s			S
860 s	860 s		I
850 s	850 s	850 vs	K, D
		820 s	D
815 s	815 s		I
760 s	765 sh		I
740 s	740 s	740 s	I, D
690 sh	690 m	700 sh	K
620 vw			S
590 s	585 m		I
520 m	530 w	528 m	I, D
510 m	500 sh	495 m	I
		460 m	K
450 w	450 vw		D
			I

^a after 11 minutes, ^b 18 hours, ^c 21 days of isothermal decomposition in self-generated atmosphere, ^d absorption bands represent $\nu(V-O)$, $\nu(O-O)$, $\delta(V-O-H)$ vibrations of the these compounds. S – starting complex $K_3[OH(VO(O_2)_2)_2] \cdot H_2O$, K – KVO_3 , I – $K_4[V_2O_6(O_2)] \cdot 3H_2O$, D – $K_4V_2O_7$

Table 3 X-ray powder patterns of the $K_3[OH\{VO(O_2)_2\}_2] \cdot H_2O$ (S), of the decomposition products after 11 minutes (P₁), 21 days (P_F) in self-generated atmosphere, $K_4[V_2O_6(O_2)] \cdot 3H_2O$ and $K_4V_2O_7$ (D)

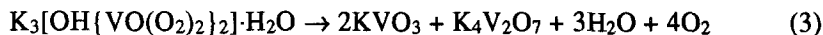
S		P ₁		P _F		K ₄ [V ₂ O ₆ (O ₂)]·3H ₂ O ^a		D ^a	
<i>d</i> / nm	<i>I</i>	<i>d</i> / nm	<i>I</i>	<i>d</i> / nm	<i>I</i>	<i>d</i> / nm	<i>I</i>	<i>d</i> / nm	<i>I</i>
0.544	95	0.548	10						
0.517	15			0.505	6 ^b				
		0.493	11			0.491	12	0.489	11
0.486	35			0.487	7			0.486	11
		0.472	7						
				0.460	9	0.464	10	0.461	8
		0.411	7	0.403	10	0.407	10	0.404	12
				0.386	7 ^b				
				0.368	8 ^b				
0.356	16	0.359	4			0.360	5		
0.346	27	0.347	55			0.344	5		
				0.336	9			0.337	17
0.329	100	0.332	15					0.324	9
0.322	48	0.316	37			0.312	33	0.312	25
0.308	57	0.310	100 ^b	0.308	65 ^b	0.307	100		
				0.304	100			0.305	100
0.297	19								
		0.293	35			0.289	65	0.291	11
				0.285	57			0.286	74
		0.283	9 ^b	0.281	25 ^b			0.279	11
0.277	11	0.275	5			0.273	15		
				0.267	5			0.268	13
0.260	17	0.260	11 ^b	0.259	10 ^b			0.259	7
0.252	17								
0.243	19	0.244	5 ^b	0.241	8 ^b			0.244	7
		0.236	12 ^b	0.232	19 ^b	0.233	21	0.232	20
0.228	25	0.229	7					0.221	6
0.215	16	0.215	5						
		0.205	9	0.203	18	0.204	22	0.202	20
		0.198	5 ^b	0.194	7 ^b				

^a Our results. ^b Also diffraction lines of KVO₃ [3]



The IR spectrum of the product formed when heating was interrupted at 188°C (Fig. 2b) exhibits the absorption bands of $\text{K}_4[\text{V}_2\text{O}_6(\text{O}_2)]\cdot 3\text{H}_2\text{O}$ and KVO_3 . This is also supported by diffraction patterns (Table 1) and chemical analyses (28.8% V(V), 4.7% O_2^{2-}), which indicate that the final products obtained are $\text{K}_4[\text{V}_2\text{O}_6(\text{O}_2)]\cdot 3\text{H}_2\text{O}$ and KVO_3 (calc. for 1:2 mixture: 28.3% V(V), 4.4% O_2^{2-}).

The second step on the TG curve, accompanied by an exothermic effect with maximum at 215°C, corresponds to total peroxy oxygen loss from the $\text{K}_4[\text{V}_2\text{O}_6(\text{O}_2)]$ intermediate and $\text{K}_4\text{V}_2\text{O}_7$ is thus formed. The elemental analysis, the IR spectrum (Fig. 2c) and the X-ray diffraction patterns (Table 1)) confirm that the final products of thermal decomposition at 350°C are $\text{K}_4\text{V}_2\text{O}_7$ and KVO_3 (calc. for 1:2 $\text{K}_4\text{V}_2\text{O}_7/\text{KVO}_3$ mixture: 31.5% V(V), 36.3% K; found: 31.1% V(V), 35.8% K). The stoichiometry of the thermal decomposition under dynamic conditions up to 350°C, may be summarized as given by Eq. (3)



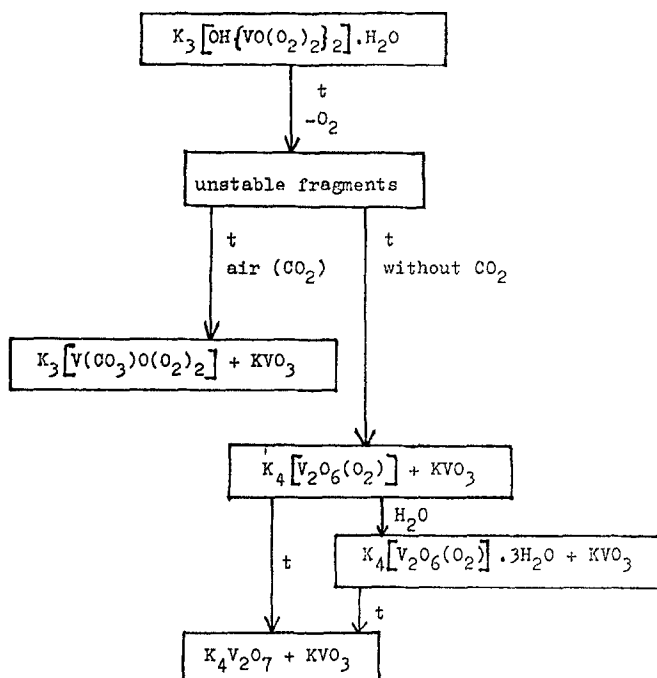
The weight loss found experimentally from the TG curve (22.2%) corresponds to that calculated from Eq. (3) (22.0%).

The IR spectra (Table 2) and X-ray diffraction patterns (Table 3) of the products of isothermal decomposition of $\text{K}_3[\text{OH}\{\text{VO}(\text{O}_2)_2\}_2]\cdot\text{H}_2\text{O}$ in a self-generated atmosphere confirm the course of decomposition as proposed by Eqs (2) and (3). The results of elemental analysis and the composition of decomposition products based on phase analysis (the IR spectra and X-ray diffraction patterns) are given in Table 4.

The results, both obtained in the study presented here and in [1] enabled us to describe the course of thermal decomposition of $\text{K}_3[\text{OH}\{\text{VO}(\text{O}_2)_2\}_2]\cdot\text{H}_2\text{O}$ by Scheme 1. After partial release of oxygen from the coordinated peroxy groups and release of water, the coordinatively unsaturated fragments are formed. The completion of coordination polyhedron can proceed in two ways:

(i) if the reaction is slow enough (the decomposition at low temperatures) and proceeds in the presence of CO_2 , by formation of the $\text{K}_3[\text{V}(\text{CO}_3)\text{O}(\text{O}_2)_2]-\text{KVO}_3$ mixture.

* Composition proposed. As the composition of the decomposition products was estimated after cooling to room temperature, the intermediate which gives on cooling the $\text{K}_4[\text{V}_2\text{O}_6(\text{O}_2)]\cdot\text{H}_2\text{O}$ complex cannot be satisfactorily identified. $\text{K}_4[\text{V}_2\text{O}_6(\text{O}_2)]\cdot 3\text{H}_2\text{O}$ was prepared as a pure substance by thermal decomposition of $\text{K}_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]\cdot\text{H}_2\text{O}_2$ [2] and characterized by chemical analysis, X-ray diffraction patterns and by IR spectroscopy.



(ii) if the reaction is fast (under dynamic conditions) or proceeds under conditions when the fragments formed do not react with carbon dioxide, i.e. in a self-generated atmosphere, by formation of the intermediate $K_4[V_2O_6(O_2)]$ - KVO_3 mixture. The $K_4[V_2O_6(O_2)]$ complex then decomposes in the next step to $K_4V_2O_7$ and oxygen.

Table 4 Elemental and phase analyses of some products of the isothermal decomposition of $K_3[OH\{VO(O_2)_2\}_2] \cdot H_2O$

Time of decomposition	%			Phase analysis ^a
	V (V)	O ₂ ²⁻	Δm	
0	24.8	31.2	0.0	S
5 minutes	27.1	21.1	4.8	S+ I + K
11 minutes	30.1	8.9	12.3	S + I + K
18 hours	30.7	4.0	16.4	I + K
21 days	30.8	0.0	21.6	D + K

^a S - $K_3[OH\{VO(O_2)_2\}_2] \cdot H_2O$, I - $K_4[V_2O_6(O_2)] \cdot 3H_2O$, K - KVO_3 , D - $K_4V_2O_7$

References

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Zusammenfassung — Unter dynamischen Bedingungen bis 350°C und isotherm bei 1503°C in selbsterzeugter Atmosphäre wurde die thermische Zersetzung von $K_3[OH\{VO(O_2)_2\}_2]H_2O$ untersucht. Als Zwischenprodukt der Reaktion wird $K_4[V_2O_6(O_2)]$ gebildet. Die Endzersetzungserzeugnisse von $K_3[OH\{VO(O_2)_2\}_2]H_2O$ sind KVO_3 und $K_4V_2O_7$.