

THERMAL DECOMPOSITION OF POTASSIUM CARBONATOOXOPEROXOVANADATE(V)

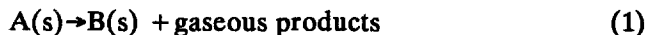
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(Received March 12, 1990)

The thermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ was studied under isothermal, dynamic and quasi-isobaric-isothermal condition. A mixture of $K_4V_2O_7$ and K_2CO_3 was identified as the primary product of thermal decomposition. Under experimental conditions not allowing a continuous loss of volatile products, the reaction of $K_4V_2O_7$ with CO_2 gives KVO_3 and K_2CO_3 .

In some recent studies, the thermal decomposition of peroxo complexes of transition metals was characterized as a process in which, after the release of oxygen from the coordinated peroxo groups, the corresponding non-peroxidic compound is formed [1-3]. The following general scheme was proposed for the thermal decomposition of peroxo complexes [1]:



As part of our systematic study of the thermal decomposition of vanadium(V) peroxo complexes, we have examined the slow thermal decomposition of mono- and dimeric oxoperoxovanadates(V) with coordinated mono- (F, H_2O , NH_3) [4-7] and bidentate ($C_2O_4^{2-}$) [8, 9] ligands.

We have found that only the thermal decomposition of $NH_4[V(NH_3)O(O_2)_2]$ [5] proceeds according to Scheme (1). If some other anionic ligand (F, $C_2O_4^{2-}$) is bound to the vanadium(V) in an oxoperoxocomplex, the thermal decomposition of such a compound always results in the formation of a mixture of vanadate (KVO_3) with a compound containing an anionic ligand ($K_3VF_4O_2$, $K_2VF_3O_2$, $K_2C_2O_4$).

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$K_3[V(CO_3)O(O_2)_2]$ belongs in the group of complexes of the type $M^I[VO(O_2)_2LL]$, where LL is a bidentate anionic ligand. The reason why the estimation of the stoichiometry of its thermal decomposition is interesting is that the complex is also formed as a product of thermal decomposition of $K_4[V_2O_3(O_2)_4] \cdot H_2O$ [10], $K_3[V_2(OH)O_2(O_2)_4 \cdot H_2O$ [10] and $K_2[VFO(O_2)_2]$ [4].

Experimental

$K_3[V(CO_3)O(O_2)_2]$ was prepared according to [11]. The compound is stable at room temperature. Its weight, chemical composition and IR spectrum did not change even after heating for 14 days at 130° .

Analyses for $K_3[V(CO_3)O(O_2)_2]$ ($M = 308.2$): calc.: 16.5% V, 38.1% K, 20.7% O_2^{2-} , 3.8% C; found: 16.5% V, 38.5% K, 20.3% O_2^{2-} , 3.9% C. Vanadium was estimated by titration with $FeSO_4$. The peroxidic oxygen was previously released from the analyzed sample by heating. Peroxidic oxygen was estimated potentiometrically with $KMnO_4$. Potassium was determined by using a Flapho 4 flame photometer (Zeiss, Jena). The thermoanalytical curves were registered on a Q-1500 D derivatograph (MOM, Budapest); conditions: sample weight 400 mg, heating rate 2.5 deg/min, temperature range $20-340^\circ$. The TG curve under quasi-isobaric-isothermal conditions was registered with the use of a labyrinth crucible (sample weight 400 mg, heating rate I, temperature up to 300°).

The thermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ proceeding isothermally at $149 \pm 3^\circ$ was studied for (a) 40 days in an air atmosphere (series A), and (b) 11 days, the complex being covered in a Petri dish (series B). The temperature of $149 \pm 3^\circ$ was found experimentally to be the lowest temperature at which any mass loss occurred after 24 hours. The course of the thermal reactions was followed by means of weight loss measurements, elemental analyses of solid intermediates, infrared spectroscopy and X-ray powder patterns. The X-ray diffraction patterns were obtained on a Philips diffractometer equipped with a PW 1050 goniometer; $CuK\alpha$ radiation was used. The IR spectra in Nujol mulls were registered on Specord M 80 or Perkin-Elmer 180 spectrophotometers.

Results and discussion

The IR bands of the products of isothermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ in air atmosphere (series A) are shown in Table 1. The IR spectrum of the product obtained after 28 days of decomposition (P₂₈) exhibits the absorption bands of $K_3[V(CO_3)O(O_2)_2]$, $K_4V_2O_7$ and K_2CO_3 .

Table 1 Vibrational spectra of the products of isothermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ (series A) ($1200\text{--}400\text{ cm}^{-1}$)

P ₂₈ ^a	P ₄₀ ^b	P ₄₀ ^c	Assignment
1058 m		1055 m	K_2CO_3
1048 m			$K_3[V(CO_3)O(O_2)_2]$
	1028 w		K_2CO_3
		965 s	KVO_3
936 s		935 sh	KVO_3 , $K_3[V(CO_3)O(O_2)_2]$
925 sh	925 vs	925 s	$K_4V_2O_7$
		890 w	KVO_3
888 w	880 vs	880 s	$K_4V_2O_7$
860 s			$K_3[V(CO_3)O(O_2)_2]$
	850 vs	855 s	$K_4V_2O_7$, KVO_3
820 w	820 vs		$K_4V_2O_7$
740 sh	740 vs	740 s	$K_4V_2O_7$
		690 w	KVO_3 , K_2CO_3
670 w	666 m	670 vw	K_2CO_3
626 m			$K_3[V(CO_3)O(O_2)_2]$
586 m			$K_3[V(CO_3)O(O_2)_2]$
530 sh	520 w	520 w	$K_4V_2O_7$
486 w			$K_3[V(CO_3)O(O_2)_2]$
	460 m	466 w	$K_4V_2O_7$
445 m			M [*]

* Unknown intermediate

^a After 28 days

^b After 40 days of decomposition

^c The final product after six months above silica gel in a desiccator

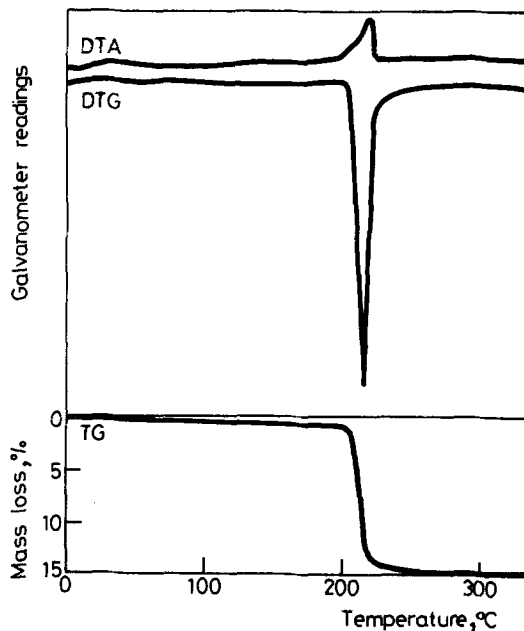


Fig. 1 Thermoanalytical curves of $K_3[V(CO_3)O(O_2)_2]$

The IR spectrum exhibits a relatively strong band at 445 cm^{-1} , the intensity of which decreases during the decomposition. We presume that this band is connected with the formation of an unknown intermediate. In the IR spectrum of the final product of decomposition (P₄₀), after 40 days of decomposition, only the bands of $K_4V_2O_7$ and K_2CO_3 can be observed. These IR spectroscopic results are supported by the diffraction patterns.

The thermoanalytical curves of $K_3[V(CO_3)O(O_2)_2]$ under dynamic conditions up to 340° , are shown in Fig. 1. The weight loss starts at a temperature above 200° . The decomposition of the complex is manifested in the DTA curve by an asymmetric exothermic peak ($t_{\max} = 221^\circ$). The IR spectrum (Fig. 2) and the X-ray pattern (Table 2) indicate that the product of decomposition is a mixture of $K_4V_2O_7$ and K_2CO_3 .

The stoichiometry of thermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ under dynamic conditions up to 340° , and also under isothermal conditions (series A), can be described by the equation

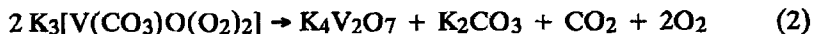


Table 2 X-ray powder patterns of the decomposition products of $K_3[V(CO_3)O(O_2)_2]$ (series A and B) and of the product of thermal analysis interrupted at $340^\circ C$ (TA)

Series A (40) ^a			$K_3[V(CO_3)O(O_2)_2]^{[4]}$			$KVO_3^{[12]}$			$K_2V_2O_7^b$			$K_2CO_3^{[12]}$			Series B (11)		
<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>	<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>
0.487	10	0.488	13	0.582	29	0.512	11					0.579	38	0.511	8	0.489	11
0.463	7			0.477	43			0.461	8			0.477	55	0.468	8	0.461	8
				0.468	35							0.460	38	0.461	8	0.458	48
				0.463	27			0.461	8			0.458	48	0.431	15	0.404	15
				0.458	28			0.404	12								
				0.422	17												
0.404	16	0.404	11					0.390	8			0.375	38	0.370	10	0.363	9
				0.371	36			0.371	6					0.363	9	0.335	10
								0.364	15								
0.337	11	0.337	11														
				0.326	50			0.337	17			0.327	65	0.315	11	0.305	100
0.312	15	0.312	25	0.311	100	0.311	100	0.312	25			0.313	100	0.315	11	0.305	100
0.305	100	0.304	100	0.305	32			0.305	100			0.304	50	0.305	100		
0.294	15			0.295	18							0.297	16				
								0.291	10								
0.286	80	0.285	90	0.288	22			0.286	74			0.289	26	0.289	70	0.280	35
0.279	29	0.280	47	0.282	45	0.282	32					0.283	27	0.280	35	0.276	46
				0.276	46			0.279	11			0.279	87	0.276	46		
				0.266	20			0.268	13			0.268	20	0.260	7		
0.259	10					0.260	20	0.259	7					0.260	7		
0.243	4			0.241	23	0.243	11	0.244	7			0.242	20	0.244	7		
0.236	5	0.232	18	0.235	30			0.244	7			0.234	70	0.233	23		
												0.237	16				

^a The day of decomposition is in parentheses; ^b Our result.

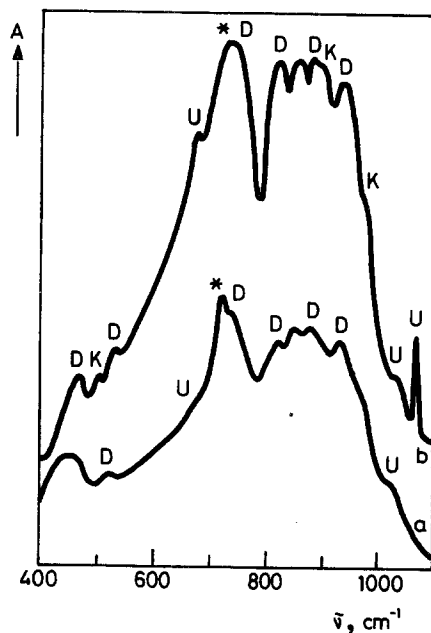


Fig. 2 IR spectra of the final product of thermal decomposition up to 340°C (a) and the product after registration of the TG curve under quasi-isobaric-isothermal conditions (b)

The weight losses calculated from the TG curve (15.6%) and found experimentally in the isothermal decomposition in series A (16.9%) are smaller than that corresponding to the decomposition of $K_3[V(CO_3)O(O_2)_2]$ according to Eq. (2) (calc. 17.5%). The contents of vanadium(V) estimated in the final products of decomposition (18.7% and 18.4%) are also smaller than that calculated for a 1:1 mixture of $K_4V_2O_7$ and K_2CO_3 (20.0%). The reason why these experimentally found values are smaller than expected is probably the fact that both components of the mixture ($K_4V_2O_7$ and K_2CO_3) are hygroscopic, e.g. the corresponding hydrates of the reaction products are formed. Obviously, the formation of crystallohydrates also causes the shift of the IR bands of K_2CO_3 in the IR spectra of the intermediates and the final products of decomposition (from 1028 to 1063 cm^{-1} and from 675 to 697 cm^{-1}).

Figure 3 shows the IR spectra of the intermediates and the final product of thermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ proceeding isothermally (series B, in a covered Petri dish). The IR spectrum measured at the beginning of decomposition, similarly as in series A, exhibits a band at 445 cm^{-1} .

Thus, the IR spectra indicate that KVO_3 , $\text{K}_4\text{V}_2\text{O}_7$ and K_2CO_3 are present in the products of decomposition. The results of chemical analysis and the composition of the decomposition products based on the IR spectra and diffraction patterns (Table 2) are presented in Table 3. The TG curve measured under quasi-isobaric-isothermal conditions is shown in Fig. 4. The IR spectrum of the decomposition product (Fig. 4) confirms that the product obtained contains not only $\text{K}_4\text{V}_2\text{O}_7$ and K_2CO_3 , but also KVO_3 .

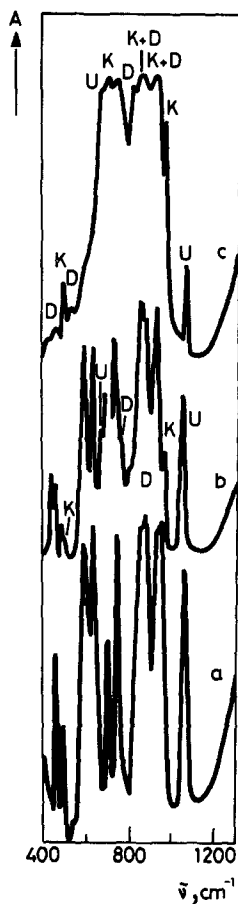


Fig. 3 IR spectra of $\text{K}_3[\text{V}(\text{CO}_3)\text{O}(\text{O}_2)_2]$ (a), and the decomposition products after 4 days (b) and 11 days (c) (series B). D - $\text{K}_4\text{V}_2\text{O}_7$, K - KVO_3 , U - K_2CO_3

Table 3 Elemental and phase analyses of some intermediates of the isothermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ (series B)

Day of decomp.	Weight loss, %	V %	O_2^{2-} %	C %	Phase analyses
0	0	16.5	20.3	3.9	P*
4	5.4	16.9	14.4	3.8	P, M**, K_2CO_3 , KVO_3 , $K_4V_2O_7$
5	8.4	17.2	12.6	4.2	P, M, K_2CO_3 , KVO_3 , $K_4V_2O_7$
6	10.2	16.7	10.7	4.7	P, M, K_2CO_3 , KVO_3 , $K_4V_2O_7$
8	14.1	17.0	5.9	5.6	P, K_2CO_3 , KVO_3 , $K_4V_2O_7$
9	16.0	17.4	2.0	5.0	P, K_2CO_3 , KVO_3 , $K_4V_2O_7$
11	16.5	17.3	0.0	5.3	K_2CO_3 , KVO_3 , $K_4V_2O_7$

*Starting complex $K_3[V(CO_3)O(O_2)_2]$.

**Unknown intermediate

The fundamental difference between series A and series B is the presence of KVO_3 in the intermediates and in the final product of decomposition in the latter series. KVO_3 is not the primary product of decomposition, but is probably formed in the reaction

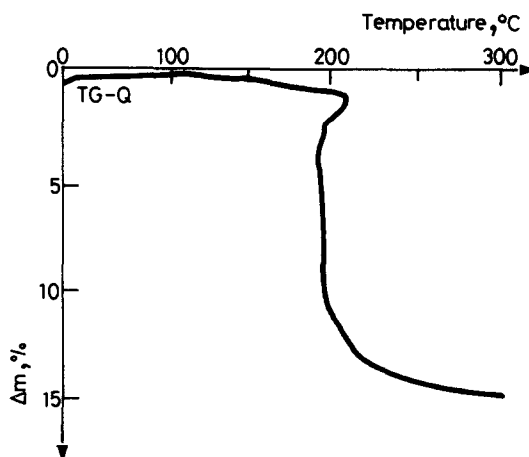
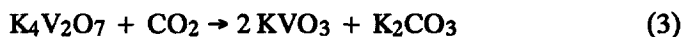


Fig. 4 TG curve measured under quasi-isobaric-isothermal conditions

The rate of this reaction at room temperature is slow if the $K_4V_2O_7$ is kept above silica gel in a desiccator. Similar significant changes occurred in the spectrum of the final product of decomposition of $K_3[V(CO_3)O(O_2)_2]$ in series A ($K_4V_2O_7 + K_2CO_3$) when the complex was kept above silica gel for six months at room temperature. The IR spectrum of this product (Table 1) exhibits characteristic bands of $K_4V_2O_7$, K_2CO_3 and KVO_3 . The decomposition of $K_3[V(CO_3)O(O_2)_2]$ (series B) is accompanied by an increase in the carbon content (Table 3), which can be explained by the successive course of reactions (2) and (3).

The results obtained show that the thermal decomposition of $K_3[V(CO_3)O(O_2)_2]$ proceeds according to Eq. (2), and $K_4V_2O_7$ is formed as the primary product of decomposition. Under experimental conditions not allowing the continuous loss of volatile products of decomposition (the sample in series B is kept closed in a Petri dish, with quasi-isobaric-isothermal conditions during TG measurements), $K_4V_2O_7$ is transformed to KVO_3 according to Eq. (3).

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Zusammenfassung — Unter isothermen, dynamischen und quasi-isobaren Bedingungen wurde die thermische Zersetzung von $K_3[V(CO_3)O(O_2)_2]$ untersucht. Als Primärprodukt der thermischen Zersetzungsreaktion wurde ein Gemisch aus $K_4V_2O_7$ und K_2CO_3 festgestellt. Wird unter experimentellen Bedingungen das Entweichen flüchtiger Produkte verhindert, so gibt die Reaktion von $K_4V_2O_7$ mit CO_2 die Produkte KVO_3 und K_2CO_3 .