Thermochimica Acta, 184 (1991) 213–219
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition of potassium fluorooxodiperoxovanadate(V)

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(Received 7 November 1990)

Abstract

The thermal decomposition of $K_2[VFO(O_2)_2]$, proceeding isothermally at 114 and 175 °C in a self-generated atmosphere or under dynamic conditions up to 240 °C, is a multi-step process. The unstable intermediate formed in the first stage of the decomposition reacts to form a mixture of KVO_3, KF, $K_3VF_4O_2$ and $K_4[V_2O_6(O_2)]$. The final decomposition product is a mixture of $K_4V_2O_7$, KVO_3, $K_3VF_4O_2$ and KF.

INTRODUCTION

The different types of fluorooxo compounds of vanadium(V), e.g. M^IVF_4O, $M^I_2VF_5O$, $M^I_3VF_4O_2$, $M^I_2VF_3O_2$ and $M^IVF_2O_2$, can be prepared by solid phase reactions and also by crystallisation from aqueous solutions. A new method of synthesis of fluorooxo complexes of vanadium(V) and other transition metals, Zr(IV), Ti(IV), Nb(V) and Ta(V), has been proposed: the thermal decomposition of the corresponding fluorooxoperoxo complexes [1,2] in which it has been proved experimentally that all the compounds lose mass corresponding only to the release of oxygen from the coordinated peroxo ligand. For example, the thermal decomposition of $K_2[VFO(O_2)_2]$ is accompanied by a weight loss which is in accordance with the formation of the new compound, K_2VFO_3 [3]. The products of the thermal decomposition of these fluorooxo complexes have not been characterised by other physicochemical methods [1].

The several simultaneous reactions proceeding during the isothermal decomposition of $K_2[VF(O_2)_2]$ in a CO_2-containing atmosphere always result in formation of a mixture of KVO_3, $K_3[V(CO_3)O(O_2)_2]$, $K_3VO_2F_4$ and other compounds, K_2CO_3 and/or hydrated $K_4[V_2O_6(O_2)]$ [4].

This paper deals with the thermal decomposition of $K_2[VFO(O_2)_2]$ under conditions when the intermediates formed do not react with carbon dioxide.

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0040-6031/91/$03.50

The thermal decomposition was studied to determine whether or not it can be exploited in the synthesis of K_2VFO_3.

EXPERIMENTAL

$K_2[VFO(O_2)_2]$ was prepared according to ref, 5. Analysis: calc., 22.31% V, 28.05% O_2^{2-}, 8.30% F; found, 22.2% V, 28.1% O_2^{2-}, 8.5% F.

$K_3VF_4O_2$ was prepared by solid phase reaction: 1.38 g (10 mmol) of KVO_3 and 1.56 g (20 mmol) of KHF_2 were powdered in an agate mortar and heated at 150 ° C for 4 hours in a platinum crucible. Analysis: calc., 18.4% V, 27.5% F; found, 18.2% V, 27.9% F. The methods of elemental analysis used were described in our previous paper [6]. The thermoanalytical curves were recorded on a Derivatograph Q-1500 D (MOM, Budapest). The X-ray powder diffraction patterns were recorded using a PW 1050 goniometer (Philips) and Cu Kα radiation. The IR spectra in Nujol mulls were measured on a Specord M 80 spectrophotometer (Zeiss, Jena).

The thermoanalytical curves of $K_2[VFO(O_2)_2]$ were measured up to 240 ° C under dynamic conditions (sample weight 600 mg, air atmosphere, heating rate 0.6 ° C min^{-1}). The isothermal decomposition of $K_2[VFO(O_2)_2]$, at 114 ± 3 and 175 ± 3 ° C, respectively, proceeded in a self-generated atmosphere in a glass vessel closed by a Bunsen valve. To avoid changes in the self-generated atmosphere by opening the vessel which could thus initiate further reactions of the solid decomposition products, the samples were decomposed in parallel in several vessels and the decomposition was interrupted successively on the basis of the weight loss monitored.

The data on the individual stages of the decomposition were obtained from the IR spectra, chemical analyses and the diffraction patterns of the products formed when the thermal decomposition was interrupted at 170 and 183° C, and from the XRD patterns and the IR spectra of the series of products of the isothermal decomposition of $K_2[VFO(O_2)_2]$ in a self-generated atmosphere. The decomposition products were analysed immediately after cooling to room temperature in a desiccator above KOH.

RESULTS AND DISCUSSION

The weight loss, 14%, calculated from the TG curve of $K_2[VFO(O_2)_2]$ (Fig. 1) corresponds to release of oxygen from the coordinated peroxo ligands and is in excellent agreement with the value, $\Delta m = 14.0\%$, calculated from [3]

$$K_2[VFO(O_2)_2] \xrightarrow{t} K_2VFO_3 + O_2 \qquad (1)$$

Nevertheless, the two exothermic peaks on the DTA curve with maxima at 172 and 192° C, indicate that oxygen is released in two steps.

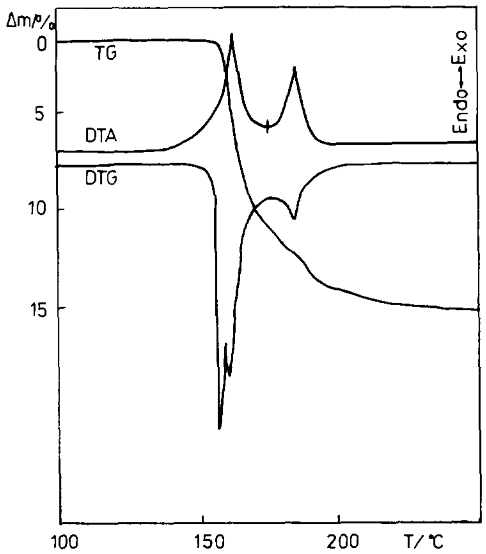


Fig. 1. Thermoanalytical curves of $K_2[VFO(O_2)_2]$.

In the first stage of decomposition, the unstable intermediate, M_x, is formed after a partial release of oxygen from the coordinated peroxo groups. The composition of M_x could not be estimated by chemical analysis, as it was obtained only in the mixture with the starting complex. The formation of M_x during isothermal decomposition in a self-generated atmosphere can be studied readily by IR spectroscopy (Fig. 2). The characteristic absorptions for M_x at 930 cm^{-1} (ν(V=O) and $\nu(O_p–O_p)$, where O_p is peroxidic oxygen), 740 cm^{-1} (ν(V–O–V)?) and at 605 and 560 cm^{-1} ($\nu(V–O_p)$?), indicate that M_x is a monoperoxo complex which can be formulated as $K_2[VFO_2(O_2)]$. The product of thermal decomposition obtained when heating was interrupted at 170 °C, a temperature almost identical with the first exothermic maximum on the DTA curve, is also a mixture of M_x with the starting complex ($P^{\star}_{170}$, Table 1). M_x is so unstable that it decomposes during the X-ray measurement ($P^{\star\star}_{170}$, Table 1).

In the next step of the thermal decomposition of $K_2[VFO(O_2)_2]$, the formation of several compounds was observed. The product obtained when heating was interrupted at 183 °C, i.e. between the two exothermic effects, still contains peroxidic oxygen (Δm = 9.8%, 24.3% V, 4.7% O_2^{2-} and 9.1% F) and its IR spectrum exhibits absorptions of KVO_3, $K_3VF_4O_2$ and $K_4[V_2O_6(O_2)] \cdot 3H_2O$. $K_4[V_2O_6(O_2)] \cdot 3H_2O$ was obtained as a pure substance when the intermediate formed on decomposition of $K_4[V_2O_3(O_2)_4] \cdot H_2O$ was cooled [7].) The diffraction pattern (Table 2) indicates that besides these compounds, KF is also present in the mixture. The first exothermic peak on the DTA curve, with a maximum at 172 °C, corresponds to the first two steps of decomposition, i.e. the decomposition of $K_2[VFO(O_2)_2]$ to M_x and the formation of the mixture of KVO_3, $K_3VF_2O_4$ and $K_4[V_2O_6(O_2)]$.

TABLE 1

Absorption bands in the IR spectra (1050–600 cm^{-1}) of some decomposition products of $K_2[VFO(O_2)_2]$

$P^{\star}_{170}$ [a]	$P^{\star\star}_{170}$ [b]	$P^{\star\star\star}_{183}$ [c]	Assignment	P_{final} [d]	Assignment
	1045 sh[e]				
	960 sh	960 s	KVO_3	960 sh	KVO_3
945 s			$K_2[VFO(O_2)_2]$		
930 s			M_x		
	920 s	925 vs, b	$K_4[V_2O_6(O_2)]\cdot 3H_2O$, $K_3VF_4O_2$	930 s	$K_3VF_4O_2$, $K_4V_2O_7$
905 s			$K_2[VFO(O_2)_2]$		
	900 vs	900 s	$K_4[V_2O_6(O_2)]\cdot 3H_2O$		
875 vs			$K_2[VFO(O_2)_2]$		
	860 vs [e]	850 vs, b	$K_4[V_2O_6(O_2)]\cdot 3H_2O$, $K_3VF_4O_2$, KVO_3	860 vs	$K_3VF_4O_2$, $K_4V_2O_7$, KVO_3
	815 vs	820 s	$K_4[V_2O_6(O_2)]\cdot 3H_2O$	815 s	$K_4V_2O_7$
	780 sh	770 sh	$K_4[V_2O_6(O_2)]\cdot 3H_2O$		
740 m			M_x		
	740 vs [e]	750 sh	$K_4[V_2O_6(O_2)]\cdot 3H_2O$	730 sh	$K_4V_2O_7$
		690 sh	KVO_3	680 s	KVO_3
		645 m	$K_4[V_2O_6(O_2)]\cdot 3H_2O$		
640 m			$K_2[VFO(O_2)_2]$		
	635 m[e]	620 sh	$K_4[V_2O_6(O_2)]\cdot 3H_2O$		
605 vs			M_x		

[a] Product obtained when heating is interrupted at 170 ° C.
[b] The same product after X-ray measurement.
[c] Product obtained when heating is interrupted at 183 ° C.
[d] Final product of the isothermal decomposition at 175 ° C in self-generated atmosphere.
[e] Absorption of $K_3[V(CO_3)O(O_2)_2]$.

In the next stage of decomposition, the intermediate, $K_4[V_2O_6(O_2)]$, is decomposed to $K_4V_2O_7$, while other components of the mixture are stable under these conditions. The process is manifested on the DTA curve by the exothermic maximum at 192 ° C and by the corresponding effects on the TG and DTG curves. The final decomposition product of $K_2[VFO(O_2)_2]$ contains no peroxidic oxygen: it is a mixture of $K_4V_2O_7$, KVO_3, $K_3VF_2O_4$ and KF (Tables 1 and 2). The course of the thermal decomposition of $K_2[VFO(O_2)_2]$, under conditions when no reaction between the intermediates and carbon dioxide can take place, is relatively complicated and may be summarised

$$5K_2[VFO(O_2)_2] \xrightarrow{t} 2KVO_3 + K_4V_2O_7 + K_3VF_4O_2 + KF + 5O_2 \tag{2}$$

The thermal decomposition study showed that under the conditions used, the thermal decomposition of $K_2[VFO(O_2)_2]$ does not provide a route for the synthesis of K_2VFO_3, although the weight loss and the results of the

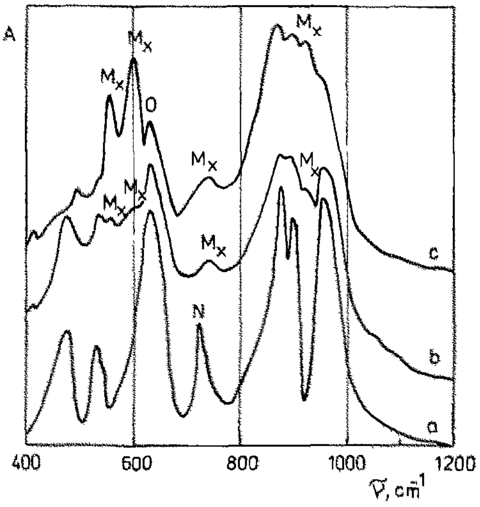
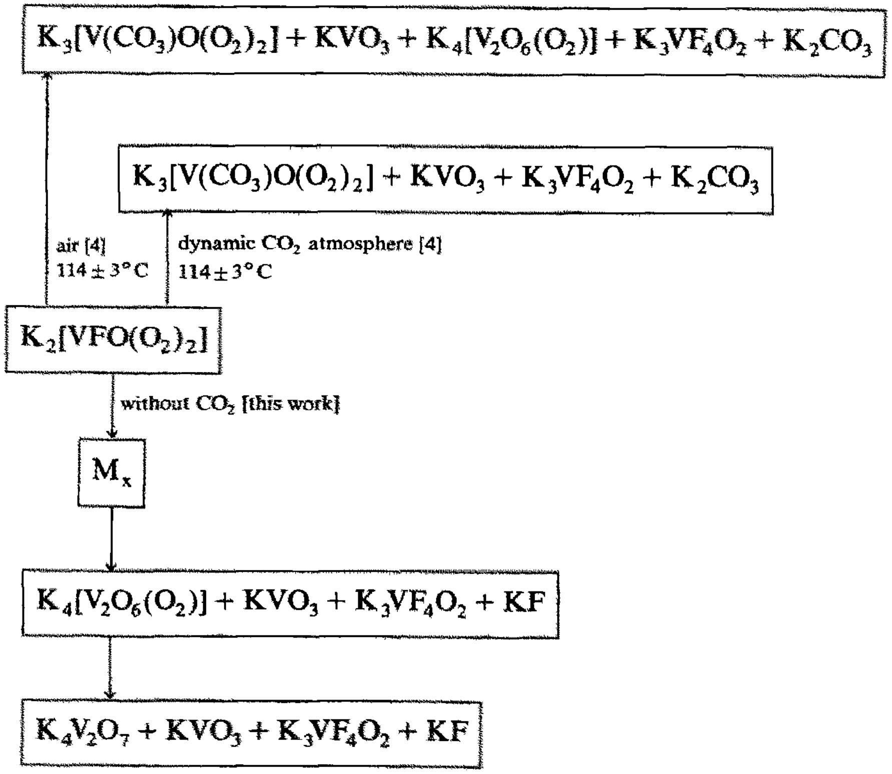


Fig. 2. Initial stages of the decomposition of $K_2[VFO(O_2)_2]$ in a self-generated atmosphere: a, IR spectrum of $K_2[VFO(O_2)_2]$; b, IR spectrum of decomposition product after 2 days; and c, after 4 days. (M_x, unstable intermediate; O, $K_2[VFO(O_2)_2]$; N, Nujol).



Scheme 1.

TABLE 2

Diffraction pattern of the product of TA interrupted at 183° C (P_{183}) and of the final product of isothermal decomposition (P_{final})

P_{183}		P_{final}		KVO_3 [8]		$K_3VF_4O_2$ [a]		$K_4[V_2O_6(O_2)]\cdot 3H_2O$ [a]		$K_4V_2O_7$ [a]	
d (nm)	I_{rel}	*d* (nm)	I_{rel}	*d* (nm)	I_{rel}	*d* (nm)	I_{rel}	*d* (nm)	I_{rel}	*d* (nm)	I_{rel}
0.515	6	0.512	31	0.512	11						
0.490	5	0.493	15			0.488	43	0.491	12	0.489	11
								0.464	10	0.461	8
0.432	27					0.426	19				
0.407	4							0.407	10		
		0.403	12							0.404	12
0.384	15	0.388	10	0.390	8						
		0.370	29	0.371	6						
		0.358	12	0.359	8						
0.310	75 [b]	0.312	61	0.311	100			0.312	33	0.312	25
0.303	100	0.307	100 [b]					0.307	100	0.305	100
		0.300	82			0.300	100				
0.290	5							0.289	65	0.291	10
0.282	3	0.282	70	0.282	32					0.286	74
0.268	7	0.271	39			0.273	4	0.273	15	0.279	11
0.265	27 [b]	0.269	20							0.268	13
		0.265	51 [b]								
0.259	10	0.260	27	0.260	20	0.257	7				
		0.257	31								
0.249	10	0.242	29	0.243	11	0.245	26			0.244	7
		0.238	11			0.239	15				
0.233	6	0.233	6					0.233	21	0.232	20
0.231	14	0.229	16	0.230	9	0.228	8				

[a] Our result.

[b] Also diffraction lines of KF [8].

chemical analyses of the final decomposition product correspond to eqns. (1) and (2).

The sequence of changes proceeding during the slow decomposition of $K_2[VFO(O_2)_2]$, in the presence of carbon dioxide [4] or in a self-generated atmosphere, is shown in Scheme 1.

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