Thermochimica Acta, 68 (1983) 297–303
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF POTASSIUM HYDROGENTETRAFLUORODIOXOTRIPEROXODIVANADATE(V) DIHYDRATE, $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$

PETER SCHWENDT and DANIELA JONIAKOVÁ

Department of Inorganic Chemistry, Comenius University, 842 15 Bratislava (Czechoslovakia)

(Received 6 April 1983)

ABSTRACT

Products of the isothermal and non-isothermal decompositions of $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$ have been studied by means of vibrational spectroscopy and X-ray phase analysis. A new peroxo complex of vanadium(V), $K_6[V_4O_4(O_2)_6F_6]$, is formed as the reaction intermediate. The final products of thermal decomposition, both isothermally at 51°C and non-isothermally up to 400°C, are KVO_3 and $K_2[VO_2F_3]$.

INTRODUCTION

In the course of the thermal decomposition of vanadium(V) peroxo complexes after partial loss of the peroxo oxygen, coordinatively unsaturated intermediate products are formed. There are two main ways of completing the coordination polyhedra: (a) formation of polymeric chains, e.g. –V–O–V– or –F–V–F–; or (b) binding of molecules from the surrounding atmosphere (CO_2, H_2O). The isothermal decomposition of $K_4[V_2O_3(O_2)_4]\cdot 2\ H_2O$ and $K_3[HV_2O_3(O_2)_4]\cdot H_2O$ at 96°C in air are examples of both (a) and (b), when in the course of decomposition the polymeric KVO_3 and $K_3[VO(O_2)_2CO_3]$ are formed [1,2].

During a systematic study of the slow decomposition of vanadium(V) peroxo complexes, which was mainly aimed at synthesis of new peroxo complexes, the thermal decomposition of a peroxo complex with a bridging peroxo group, $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$, was studied.

EXPERIMENTAL

The complex $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$ was prepared as described previously [3]. The isothermal decomposition was investigated in a static air atmosphere for 120 days at 51 ± 2°C. The course of the thermal reactions

0040-6031/83/$03.00

was followed by means of weight loss, elemental analyses of solid intermediate products, infrared and Raman spectroscopy and X-ray powder patterns. In some stages of decomposition the evolved gaseous products were absorbed in a solution and analyzed qualitatively.

The DTA and TG curves were measured with a derivatograph (system: F. Paulik, J. Paulik, L. Erdey, MOM Budapest). About 100 mg of the powdered substance was heated at a rate 2° min^{-1} in a static air atmosphere.

The IR spectra were measured in Nujol mulls using a Perkin Elmer 180 and Specord 75 IR spectrophotometers. Raman spectra were obtained using a Jeol JRS 1 spectrophotometer and a He–Ne laser. Decomposition occurred when the Ar^+ ion laser was used. X-Ray powder patterns were obtained with a Philips diffractometer (PW 1058) employing Cu K_α radiation.

Elemental analyses

Vanadium(V) was determined by titration with iron(II) sulphate after the sample had been heated for a short time to expel the peroxo oxygen. The peroxide content was estimated by potentiometric titration with potassium permanganate. Fluorine was estimated using an ion-selective electrode (Crytur 09-17) and potassium was determined by flame photometry.

RESULTS AND DISCUSSION

During the first, relatively fast stage of the isothermal decomposition of $K_3[HV_2O_2(O_2)_3F_4] \cdot 2\ H_2O$ (day 0–10, Table 1) water and hydrogen fluoride were released. Meanwhile, the content of the peroxo oxygen was rising. The release of hydrogen fluoride was proved after absorption of the gaseous decomposition products (in a sodium hydroxide solution) by reaction with Ca^{2+} ions. The stoichiometry of the first step of decomposition is given by eqns. (1) and (2).

$$\underset{\text{A}}{K_3[HV_2O_2(O_2)_3F_4] \cdot 2\ H_2O} = \underset{\text{B}}{K_3[HV_2O_2(O_2)_3F_4]} + 2\ H_2O \tag{1}$$

$$2\ \underset{\text{B}}{K_3[HV_2O_2(O_2)_3F_4]} = \underset{\text{C}}{K_6[V_4O_4(O_2)_6F_6]} + 2\ HF \tag{2}$$

Processes (1) and (2) proceeded simultaneously; the presence of anhydrous complex B in the reaction mixture was established by X-ray diffraction patterns (Table 2). The mass of the sample changed only a little between the fifth and the tenth day of decomposition and the complex $K_6[VO_4(O_2)_6F_6]$ was formed.

The decomposition of $K_6[V_4O_4(O_2)_6F_6]$ proceeded in the second step of the whole process by the release of the peroxo oxygen. In this stage of decomposition, the formation of further peroxo complex was not observed.

TABLE 1

Elemental and phase analyses of some intermediates of the isothermal decomposition of $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$

Day of decomposition	Weight loss (%)	V (%)	$(O_2)^{2-}$ (%)	F (%)	Phase analysis [a]
0	0	22.19	21.11	16.38	A
	(0) [b]	(22.14)	(20.86)	(16.51)	(A)
4	11.95	24.60	22.80	14.91	B+C
8	12.22	25.10	23.61		C
	(12.16)	(25.21)	(23.75)	(14.10)	(C)
11	12.75	25.35	19.75	15.63	C+D+E
18	14.22	25.69	17.42	15.45	C+D+E
61	20.37	27.79	3.90	16.38	C+D+E
110	22.23	28.41	0.00	15.93	D+E
	(22.59)	(28.60)	(0.00)	(16.00)	(D+E, 1 : 1)

[a] See eqns. (1)–(3) for compounds A–E.

[b] The values in parentheses are calculated for pure compounds or the mixture with the given composition.

However, after eleven days of decomposition the diffractions of the final products, KVO_3 and $K_2[VO_2F_3]$, could be found in the X-ray powder patterns. The stoichiometry of the second step of the isothermal decomposition (from the eleventh to the hundred and tenth day) is given by eqn. (3).

$$\underset{\mathrm{C}}{K_6[V_4O_4(O_2)_6F_6]} = 2\ \underset{\mathrm{D}}{KVO_3} + 2\ \underset{\mathrm{E}}{K_2[VO_2F_3]} + 3\ O_2 \qquad (3)$$

Changes in the vibrational spectra of the decomposition intermediates in various stages corresponded to eqns. (1)–(3) and were in accordance with the results of X-ray phase analysis.

The DTA and TG curves of $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$ are shown in Fig. 1. The first step on the TG curve corresponds to reactions (1) and (2). The experimental weight loss (12.25%) is in accordance with the loss of two water molecules and a molecule of hydrogen fluoride (calcd. 12.16%). On the DTA curve these reactions are expressed by an endothermic peak with a maximum at 93°C and a shoulder at 108°C. The X-ray powder pattern of an intermediate obtained by the interruption of thermal analysis at 125°C confirmed that at this stage of decomposition the complex $K_6[V_4O_4(O_2)_6F_6]$ was formed.

The second step on the TG curve, which was accompanied by a strong exothermic peak on the DTA curve with a maximum at 155°C, corresponds to the loss of all peroxo oxygen. Elemental analysis, the IR spectrum and the X-ray diffraction pattern confirmed that the final product of thermal decomposition was a mixture of KVO_3 and $K_2[VO_2F_3]$ (calcd. for 1 : 1 mixture of KVO_3 and $K_2[VO_2F_3]$: V, 28.62%; F, 16.00%; found: V, 28.49%; F, 16.28%).

TABLE 2

X-ray powder patterns of the decomposition products of $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$

A [a]		A + B (1) b		B		B + C (4) [b]		C (8) [b]		C + D + E (18) [b]		D + E (110) [b]		D [c]		E [d]	
d (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*
				0.826	42	0.823	7			0.614	25	0.616	10			0.618	29
0.748	14	0.753	14									0.564	5			0.568	61
0.610	10	0.614	18			0.616	3	0.614	25			0.515	6	0.512	11		
0.594	70	0.594	60							0.500	100						
		0.519	49	0.518	100	0.519	100			0.409	30	0.415	25			0.418	33
						0.504	10	0.501	100			0.389	10	0.389	12		
				0.476	17	0.478	7					0.371	12	0.371	13		
						0.411	3	0.411	32	0.355	15	0.350	11			0.352	12
0.399	100	0.397	100							0.346	14						
0.381	22	0.383	26							0.326	45						
0.365	8	0.367	13	0.365	29	0.363	7			0.313	80	0.313	90			0.316	74
0.344	5	0.346	24	0.346	14	0.347	35	0.348	28	0.308	64	0.311	100	0.311	100	0.310	100
		0.340	24	0.339	20	0.339	6					0.298	22			0.299	25
						0.331	4	0.329	64	0.286	20	0.283	30	0.283	98	0.286	16
						0.318	13	0.318	26			0.261	12	0.262	17	0.265	4
						0.310	4	0.310	59			0.259	14	0.258	19		
		0.306	9	0.301	38	0.301	12					0.242	12	0.243	18	0.241	14
		0.298	10	0.294	18							0.240	18	0.239	6	0.240	16
						0.290	6	0.289	21	0.226	58	0.225	32			0.226	47
0.274	24	0.275	34							0.217	35	0.220	15			0.220	14
0.232	22	0.233	40	0.237	23	0.237	8					0.217	19			0.218	30
						0.219	4	0.220	12	0.210	25	0.208	25	0.210	2	0.207	13
		0.213	34	0.211	55	0.210	14										
		0.210	17	0.208	24	0.209	14	0.208	22								
0.206	12	0.206	20														

---

[a] Designation of phases is according to eqns. (1)–(3).

[b] The day of decomposition is in parentheses.

[c] Our results.

[d] Ref. 4.

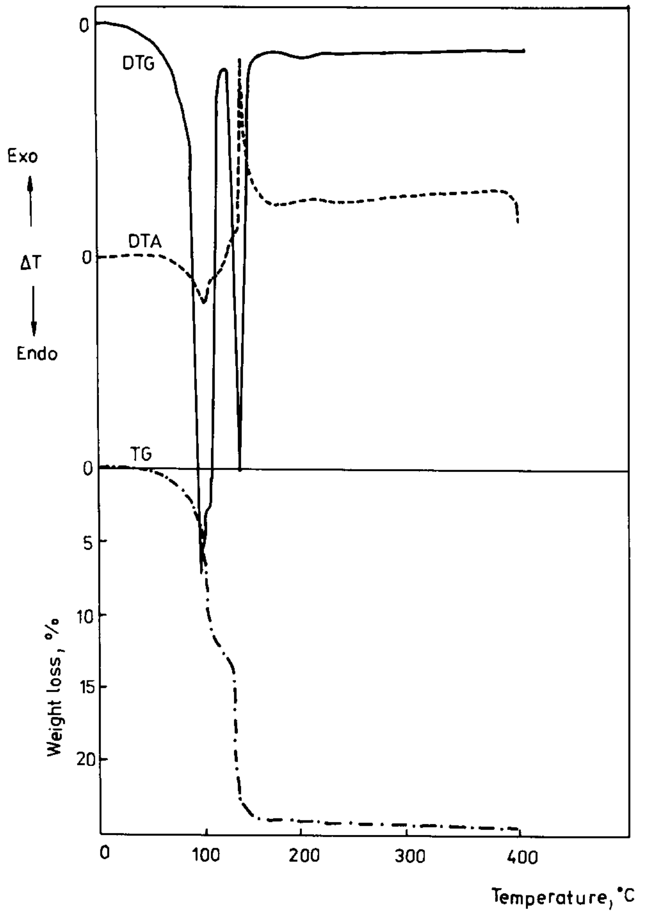


Fig. 1. DTA, TG and DTG curves for $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$.

The strong exothermic effect caused partial dispersion of the sample and therefore the experimental weight loss (23.75%) was greater than calculated (22.59%).

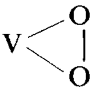
The complex $K_6[V_4O_4(O_2)_6F_6]$ represents a new peroxo complex of vanadium(V). The vibrational spectra of $K_6[V_4O_4(O_2)_6F_6]$ differ from the spectra of $K_3[HV_2O_2(O_2)_3F_4]\cdot 2\ H_2O$ mainly in the regions of V=O and V–F stretching vibrations, while the bands assigned to stretching vibrations of  groups are shifted only slightly (Table 3). Considering the proposed structure of the $[HV_2O_2(O_2)_3F_4]^{3-}$ ion [3] (Fig. 2), these changes may be interpreted in the following way: a coordinatively unsaturated intermediate is formed by the release of hydrogen fluoride from the $[HV_2O_2(O_2)_3F_4]^{3-}$ ion. Two dimeric intermediates can combine under the formation of the V–F–V bridge to a symmetrical tetrameric ion (Fig. 3). The

TABLE 3

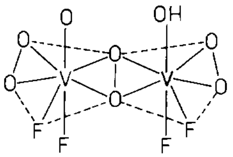
Vibrational spectra of complexes (1000–400 cm^{-1})

$K_3[HV_2O_2(O_2)_3F_4]\cdot 2H_2O$		$K_6[V_4O_4(O_2)_6F_6]$		Assignment
IR	R	IR	R	
975vs	982vs	979vs	970vs	ν(V=O)
956m	951w			δ(V–O–H)
		920vs	923m	ν(V=O)
900s	900m	900s	895w	ν(O–O)
876m	866s	856m	854s	
611s	620sh	610s	610sh	$\nu(V–O_p)$[a]
580s	584s	580s	580s	
	524s			ν(V–OH)
		520m	518m	ν(V–F)
502m	510sh	500m		
			468m	
430m	447vs	430m	404s	

[a] O_p = peroxo oxygen.

formation of new V=O and V–F–V bonds becomes evident in the vibrational spectra.

In the course of the entire isothermal decomposition one crystalline phase continuously changed into another without the formation of amorphous intermediates. Such a course of decomposition indicates that some structural similarity exists between the decomposition products and that transformation of one structural form into another does not require a great rearrangement of the coordination polyhedra. This fact is in agreement with the proposed structures of the complex anions.



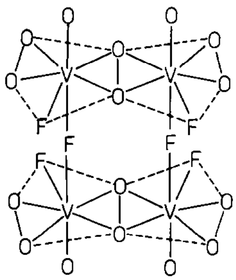


Fig. 2. The proposed structure of the $[HV_2O_2(O_2)_3F_4]^{3-}$ ion.

Fig. 3. The proposed structure of the $[V_4O_4(O_2)_6F_6]^{6-}$ ion.

REFERENCES

1 P. Schwendt and D. Úškert, Chem. Zvesti, 35 (1981) 229.

2 P. Schwendt, P. Petrovič and D. Úškert, Z. Anorg. Allg. Chem., 466 (1980) 232.

3 P. Schwendt and D. Joniaková, Proc. 9th Conf. Coord. Chem., Smolenice, ČSSR, 1983, SCHS, Bratislava, p. 367.

4 R.L. Davidovitch, T.A. Kaidalova, T.F. Levchishina and V.I. Sergiyenko, Atlas Infrakrasnykh Spectrov i Rentgenometricheskikh Dannykh Komplexnykh Ftoridov Metallov IV i V grupp, Nauka, Moscow, 1972, p. 212.