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The thermal study of vanadyl tartrates of formulae $M_x(VO)_y(L)_2 \cdot nH_2O$ (where M is Na, Sr, Ca and Ba; L is tartrate), precursors of mixed oxides

J. García-Jaca [a], M. Insausti [a], J.I.R. Larramendi [a], M.I. Arriortua [b], T. Rojo [a,*] and E. Hernández [c]

[a] *Departamento de Química Inorgánica, Universidad del País Vasco. Apdo. 644, 48080 Bilbao (Spain)*

[b] *Departamento de Mineralogía-Petrología, Universidad del País Vasco, Apdo. 644, 48080 Bilbao (Spain)*

[c] *Departamento de Física Aplicada II, Universidad del País Vasco. Apdo. 644, 48080 Bilbao (Spain)*

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Abstract

The thermal decomposition of some vanadyl tartrates of formulae $Na_4[(VO)_2(C_4H_2O_6)_2] \cdot 12H_2O$, $Ca(VO)(C_4H_4O_6)_2 \cdot 6H_2O$, $Sr(VO)(C_4H_4O_6)_2 \cdot 5H_2O$ and $[Ba_2(VO)_2(C_4H_2O_6)_2(H_2O)_8]$ have been studied by TG and DSC techniques under non-isothermal experimental conditions. All the compounds present a three-step decomposition pattern (dehydration, ligand pyrolysis and evolution of the inorganic residue), leading to a residue corresponding to several vanadates and oxides. Kinetic analyses of the dehydration curves have been performed using the Satava integral method: random nucleation, order of reaction 1.5 and the Johnson equation have given the best correlation factors. In order to obtain mixed oxides, the complexes were fired in three different atmospheres. The oxides obtained from alkaline-earth vanadyl tartrates depend on the atmosphere employed.

INTRODUCTION

Recent developments in the synthesis of high-temperature superconductors of mixed metal oxides have been mainly focused on systems containing copper [1–3]. Taking into account the relation proposed between spin one-half anti-ferromagnetic compounds and the superconductivity found for La_2CuO_4 [4], a similar behaviour [5] could be observed for a d^1 ion in a two-dimensional structure, as occurs for V(IV) in Sr_2VO_4. In this way, extensive research on Sr–V(IV)–O systems has been recently performed [6–8].

In all cases, the ceramic method was applied to obtain the different

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* Corresponding author.

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compounds, although several disadvantages associated with its utilization have been emphasized [9]. Among the alternative strategies, the method of metallo-organic precursors holds much promise because it allows for more precise control of the composition and homogeneity of the final products [10, 11]. For this reason, this work concentrates on the preparation of different precursors in the family Sr–V(IV)–O. Several complexes of formulae $M(VO)L_2 \cdot nH_2O$ (where M is Ca, Sr), $[Ba_2(VO)_2L_2(H_2O)_8]$ and $Na_4[(VO)_2L_2] \cdot 12\ H_2O$ (L is *d,l*-tartrate) are reported. This kind of compound, in which the metallic elements are dispersed but ordered, have yielded oxides whose stoichiometry can be controlled [11]. In order to determine the temperature at which the complexes decompose, as well as the decomposition stages, a detailed thermal study has been performed. In addition, the final oxides formed in the production of the inorganic degradation residues have been identified by X-ray diffraction techniques.

EXPERIMENTAL

Materials

Different complexes containing V(IV) were prepared as follows. Before the synthesis of the alkaline-earth complexes, the vanadyl tartrate dimer $Na_4[(VO)_2(C_2H_2O_6)_2] \cdot 12H_2O$ was obtained by the method of Tapscott and Belford [12]. A solution containing 734 mg (1 mmol) of this complex was mixed with a stoichiometric quantity of the alkaline-earth metal chloride aqueous solutions yielding the different compounds. The complexes were separated from the solutions as crystalline precipitates by vacuum filtration. Crystals of all the products were obtained in a diffusion device. The crystals and powder obtained were washed with water and ketone and dried over P_2O_5. In this way, the following complexes were obtained: $Na_4[(VO)_2(C_4H_2O_6)_2] \cdot 12H_2O$, $Ca(VO)(C_4H_4O_6)_2 \cdot 6H_2O$, $Sr(VO)(C_4H_4O_6)_2 \cdot 5H_2O$ and $[Ba_2(VO)_2(C_4H_2O_6)_2(H_2O)_8]$, here designated NaVOT, CaVOT, SrVOT and BaVOT respectively.

Methods

The carbon and hydrogen contents were determined by elemental analysis and the metals were analysed by atomic absorption spectroscopy (Table 1).

Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using KBr discs (2%). The thermal evolution of the complexes was investigated by TGA and DSC techniques on a Perkin-Elmer system-7 DSC–TGA. Crucibles containing 20 mg were heated at 5°C min^{-1} under a

TABLE 1

Analytical data of the complexes

Compound	Found (Calculated) (%)			
	C	H	V	M (Na, Ca, Sr, Ba)
$Na_2VC_4H_{14}O_{13}$	13.59(13.08)	3.48(3.8)	14.03(13.87)	12.73(12.54)
$CaVC_8H_{20}O_{19}$	19.08(18.78)	4.02(3.91)	10.24(9.96)	7.23(7.84)
$SrVC_8H_{18}O_{18}$	15.39(15.76)	3.15(3.33)	9.21(9.42)	16.38(16.21)
$BaVC_4H_{10}O_{11}$	11.36(11.36)	2.37(2.31)	11.78(12.05)	32.81(32.51)

dry nitrogen atmosphere. Cylindrical pellets were made from the powder using a Perkin-Elmer (PIN 15.010) hydraulic press at 5 atm pressure.

X-ray powder diffraction patterns of the final products were obtained by means of a Stoe diffractometer equipped with a germanium monochromator and using Cu Kα radiation. The diffraction positions were corrected using a separate internal standard for each compound. In order to compare the different patterns, Journal of Powder Diffraction Files (JCPDS) and theoretically generated diagrams were used. The different diagrams were indexed with the LSUCRE computer program [13].

RESULTS AND DISCUSSION

Brown prismatic crystals were obtained for all the compounds. Crystal data were determined from Weissenberg photographs with Cu Kα radiation and the final cell parameters were obtained by least-squares refinement, LSUCRE, of indexed powder diffraction patterns (Table 2). Suitable crystals of $[Ba_2(VO)_2(C_4H_2O_6)_2(H_2O)_8]$ were obtained and its structural determination performed [14].

TABLE 2

Refined cell parameters of the different complexes

Compound	NaVOT	CaVOT	SrVOT	BaVOT
Spatial group	Pbca	P2/m, P2, Pm	P2/m, P2, Pm	P$\bar{1}$
a (Å)	19.826(5)	12.335(2)	12.385(2)	7.795(1)
b (Å)	10.73(1)	10.828(2)	10.757(1)	8.496(1)
c (Å)	12.269(7)	18.364(6)	18.264(4)	8.997(1)
α (deg)	–	–	–	101.5(6)
β (deg)	–	99.98(2)	100.82(1)	68.4(9)
γ (deg)	–	–	–	96.3(8)

TABLE 3

Characteristic bands in the infrared spectra (3500–300 cm^{-1})

Compound	ν(OH)	ν(C=O)	ν_{as}(C–O) ac	δ_{ip}(O–H) alc	ν_{as}(C–O) alc	ν(VO)
Tartaric acid	3400 m	1740 s	1400 m 1390 m	1450 m	1140 m 1090 m	–
NaVOT	3610–2900 s, br	1640 s	1380 m 1320 m	–	1110 m 1080 m	950 s
CaVOT	3800–2600 s, br	1630 s	1390 m 1340 m	1410 m	1090 m 1060 m	960 s
SrVOT	3800–2600 s, br	1630 s	1390 m 1355 m	1400 m	1100 m 1060 m	980 s
BaVOT	3700–2500 s, br	1630 s	1370 m 1330 m	–	1100 m 1070 m	940–970 br

Key: ac, acid; alc, alcohol; s, strong; m, medium; br, broad.

The infrared spectra over the range 4000–600 cm^{-1} were obtained on solid samples of the different complexes. The characteristic bands for the ligand and the complexes are reported in Table 3.

The stronger bands, which appear in the 3000–2700 cm^{-1} region, are attributed to the –OH stretching vibration. Because of the low resolution of these broad bands, the O–H assignments were unsuccessful.

The region of the spectra deserving closest examination is that lying between 1550 and 1750 cm^{-1}. Complexing the carboxyl groups shifts the carbonyl band toward lower frequencies (1640–1630 cm^{-1}), while the band of the free ligand appears at 1740 cm^{-1} [15]. The variation of the ν_{as}(C–O) band, assignable to the OC–O (1390–1370 cm^{-1}) and HC–O groups (1110–1090 cm^{-1}), confirms the coordination to the metal.

The presence of a band at 1410 and 1400 cm^{-1} for the calcium and strontium compounds, respectively, corresponds to the absorption δ_{ip}(OH), which indicates the presence of hydroxyl groups. This clearly accords with the analytical results.

The bands associated with the VO vibrations appear around 960 cm^{-1}. In the case of the barium compound, a splitting of the band occurs between 970 and 940 cm^{-1}, suggesting the coordination of the oxygen in this vanadyl group. This result agrees with the crystal structure resolution [14].

The decomposition pattern of the different complexes obtained from their TG and DSC curves present three consecutive stages: dehydration, ligand pyrolysis and evolution of the inorganic residue, leading to a residual weight corresponding to complex metal oxides (Fig. 1).

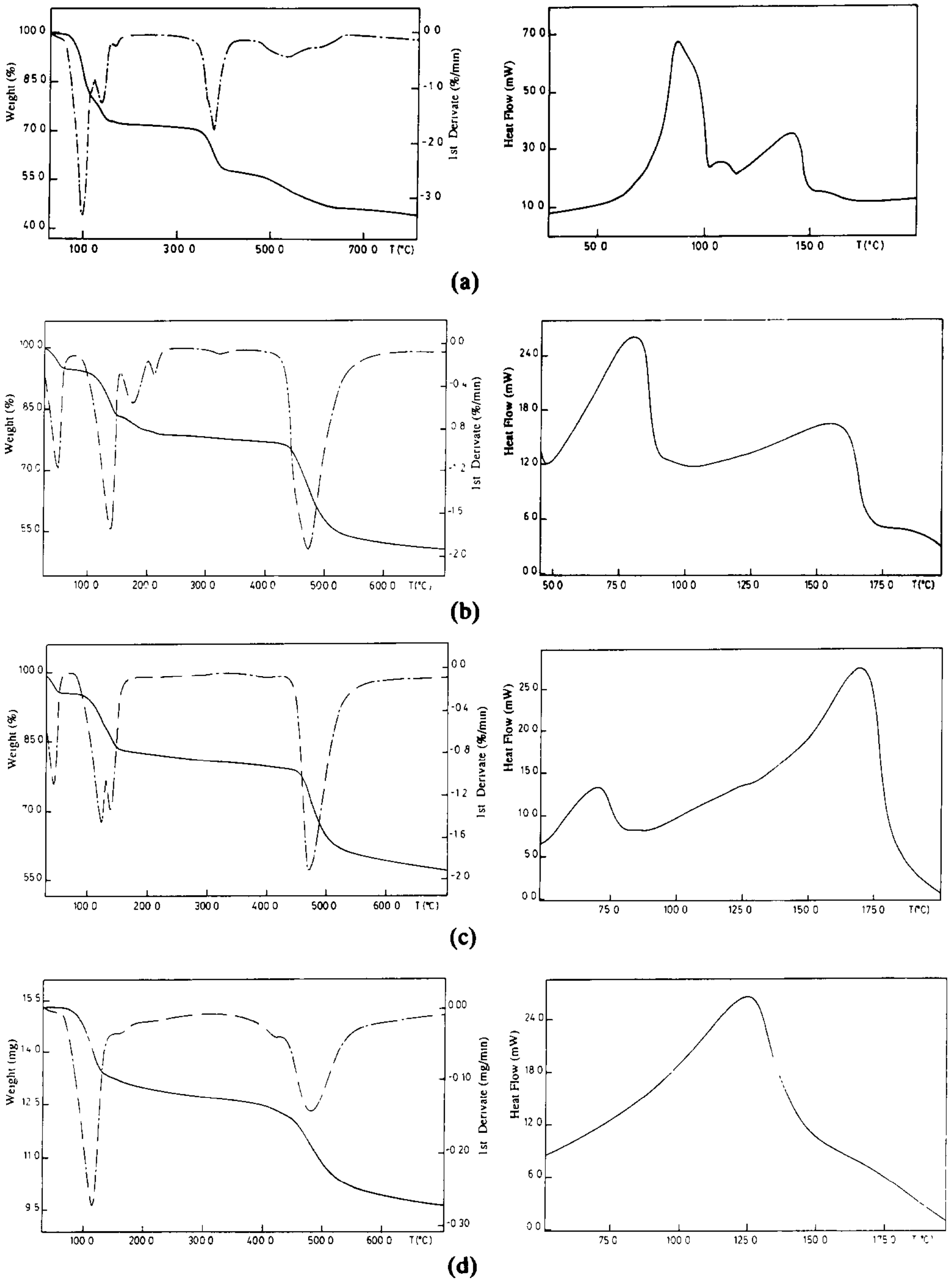

Fig. 1. TG and DSC curves for the complexes: (a) $Na_4[(VO)_2(C_4H_2O_6)_2] \cdot 12H_2O$, (b) $Ca(VO)(C_4H_4O_6)_2 \cdot 6H_2O$, (c) $Sr(VO)(C_4H_4O_6)_2 \cdot 5H_2O$, and (d) $[Ba_2(VO)_2(C_4H_2O_6)_2(H_2O)_8]$.

Dehydration

The results of the thermal studies show that the complexes are dehydrated in a single or in successive well-defined steps. The weight losses accord with the theoretical values and are summarized in Table 4.

The dehydration of the sodium compound takes place in two successive stages in the range 68–147°C, corresponding to a weight loss of 8 and 4 water molecules, respectively. In the case of the calcium and strontium compounds, the firs step occurs at low temperatures. A single well-defined stage for the barium complex suggests that the water molecules are equivalent, as can be observed in the crystal structure resolution [14].

Kinetic analysis of the dehydration curves was first performed using Satava's integral method [16]. In the cases in which different kinetic equations of the same process led to similar correlation factors, the Sharp differential method [17] was employed to obtain the best least-squares fit. The functions of random nucleation, order of reaction 1.5 and the Johnson equation gave the best fits (Table 4). The activation energy values for the calcium and strontium compounds are the maximum ones, a behaviour similar to that which has also been observed in other performed measurements.

The calorimetric measurements show the decomposition stages as sharp, exothermic peaks from which the dehydration enthalpies were calculated. These values are of the same magnitude as those previously obtained for other metallo-organic complexes [18].

TABLE 4

Thermal analysis data of the $M_x(VO)_y(L)_2 \cdot nH_2O$ compounds for the dehydration steps

Compound	H_2O molecules	Range (°C)	Weight losses (%)		Kinetic equation[a]	Activation energy (kJ mol^{-1})	ΔH (kJ mol^{-1})
			Exp.	Theor.			
NaVOT	8	68–114	19.1	19.62	NA 1	40	
	4	114–147	9.7	9.81	NA 1	25	36.5
CaVOT	2	30–59	6.3	7.02	JE	150	51.9
	3	110–152	10.6	10.52	OR 1.5	140	
	1	152–184	4.0	3.51	JE	190	
SrVOT	1	30–55	3.7	3.33	JE	210	74.0
	4	90–153	12.6	13.32	OR 1.5	100	
BaVOT	8	77–150	16.9	17.05	JE	60	43.4

[a] NA 1, random nucleation, Avrami 1; OR 1.5, order of reaction 1.5; JE, Johnson equation.

Ligand pyrolysis

After the stability interval following the dehydration, the four complexes undergo ligand pyrolysis (356–610°C), which takes place in two steps for the sodium compound and in one for the calcium, strontium and barium complexes. Therefore, it can be deduced that for the latter cases, the mixed oxide formation will occur without intermediate stable species [19]. The theoretical weight losses accompanying this degradation correspond to an oxide or vanadate M–V–O and residual evolved gases. Carbonate formation was not been observed although this has been assumed for previous pyrolysis reactions with alkaline-earth metals and acid ligands [11]. However, it is interesting to note that the ligand decomposition may involve the oxidation of V(IV) to V(V) because of the atmosphere resulting from the tartrate decomposition.

Inorganic residue evolution

An understanding of the evolution which the inorganic residue undergoes after ligand pyrolysis is required for the study of the final products. In this step, which remains stable over an interval between 500 and 800°C, different oxide precursors of superconductor phases can be formed. For this reason, the complexes were fired in tubular furnaces under several atmospheric conditions (air, nitrogen and hydrogen) and different temperatures, the resulting products being characterized by X-ray powder diffraction (Table 5).

The reaction of the sodium compound yields a mixture of phases (α-$NaVO_3$, β-$NaVO_3$) which do not depend on the atmosphere employed.

TABLE 5

Phases detected in the inorganic residue by X-ray diffraction

Atmosphere	NaVOT	CaVOT	SrVOT	BaVOT
Air	α-$NaVO_3$ β-$NaVO_3$ R(s)	$Ca_2V_2O_7$	$Sr_2V_2O_7$	$Ba_2V_2O_7$ R(s)
Nitrogen	α-$NaVO_3$ β-$NaVO_3$ R(s)	$Ca_3(VO_4)_2$ R(s)	$Sr_3(VO_4)_2$ R(s)	$Ba_3(VO_4)_2$ R(s)
Hydrogen	α-$NaVO_3$ β-$NaVO_3$ R(s)	$CaVO_3$ $Ca_3(VO_4)_2$ R(s)	$SrVO_3$ $Sr_3(VO_4)_2$ R(s)	$Ba_3(VO_4)_2$ R(s)

Key: R(s), no assigned diffraction peaks.

Nevertheless, there are some remaining unidentified diffraction peaks. In the case of the alkaline-earth vanadyl tartrates, the phases obtained do depend on the atmosphere employed.

After heating the precursors in air, pirovanadates $M_2V_2O_7$ (where M is Ca, Sr, Ba) are always found. Because vanadium (V) is present in these compounds, and because there is an absence of two-dimensionality in their structures [20], they are not suitable for superconductivity research.

Under nitrogen flux, the reaction of the complexes yield metal alkaline-earth orthovanadates, $M_3(VO_4)_2$ (where M is Ca, Sr, Ba). The V:M ratio was 1:1 in the precursors; therefore some impurities are present in the vanadium compounds, as suggested by the diffraction peaks not assigned to orthovanadates. The properties reported for the previous phases also make them unsuitable as precursor oxides.

For the thermal treatment in a hydrogen atmosphere, the presence of V(IV) phases as $SrVO_3$ and $CaVO_3$ was detected together with other vanadates. The $SrVO_3$ phase has attracted great interest because of its perovskite structure and the presence of vanadium(IV) [21]. For the barium compound, the presence of vanadium(IV) in the inorganic residue was detected by EPR measurements. Currently, improved results in the synthesis of single V(IV) phases are being achieved by modifying the different conditions of time and temperature in a hydrogen atmosphere.

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