

## **INFRARED SPECTRA AND THERMAL BEHAVIOUR OF SALTS OF THE BIS(MALONATO) OXOVANADIUM(IV) ANION**

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Infrared spectra of a series of anhydrous (Rb, Cs) and hydrated (Na, K, Ca, Sr, Ba, Pb, Ag, Tl) salts of the complex anion  $[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]^{2-}$  were recorded and briefly discussed. The thermal behaviour of these compounds, as well as that of the corresponding diprotonated ethylenediamine cation, were investigated by TG- and DTA-methods in  $\text{N}_2$ -atmosphere and complemented with studies carried out in crucible furnaces in air. Pyrolysis intermediates and residues were characterized by IR spectroscopy and overall stoichiometries for the degradation processes were proposed. In most cases orthovanadate/ $\text{VO}_2$  mixtures were obtained as final residues in  $\text{N}_2$ , whereas the corresponding divanadates were produced in air.

The vanadyl(IV) cation,  $\text{VO}^{2+}$ , is the most stable vanadium(IV) species and it dominates to a great extent the chemistry of this oxidation state [1–3]. This cation is also the most important vanadium species appearing in living systems [4, 5].

As it is known, the  $\text{VO}^{2+}$  cation prefers oxygen donor ligands [6] and a great number of complexes with carboxylate anions have been prepared and investigated in the last decades.

An interesting series of salts of the complex anion bis(malonato)oxovanadate(IV),  $[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]^{2-}$ , were prepared and characterized sixty years ago by Schramm [7] but they have not been subsequently studied by modern physicochemical methods.

As part of our present studies devoted to the synthesis and characterization of vanadyl complexes and salts of different types [8–14] we have now investigated the vibrational and thermal behaviour of a great number of salts of the above mentioned complex anion.

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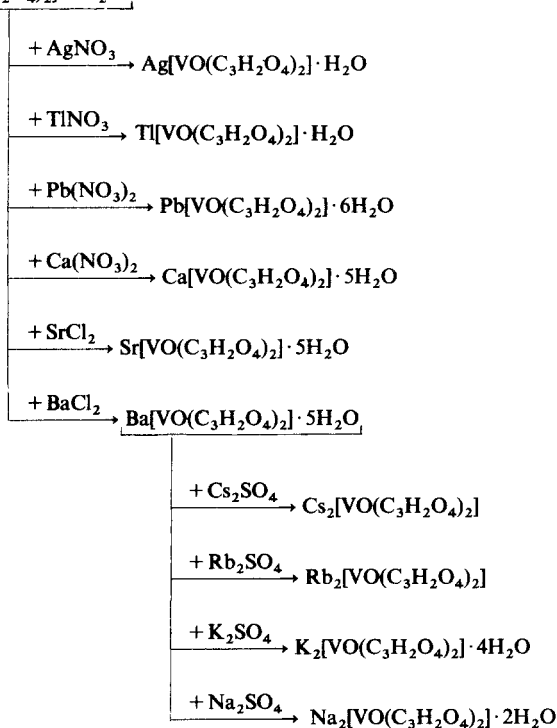
## Experimental

### Preparation of samples

The starting material for most of the preparations was the ammonium salt of the complex anion:  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ . This salt was obtained by treating  $\text{NH}_4\text{VO}_3$  with malonic acid in the presence of ammonium carbonate [7]. The most insoluble dimalonatovanadyl salts (Ag, Tl, Pb, Ca, Sr, Ba) could be obtained by double decomposition of the ammonium salt and the corresponding nitrates or chlorides of the respective cation [7]. Other salts were obtained by treating  $\text{Ba}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  with the respective metal sulfate. After the separation of the precipitated  $\text{BaSO}_4$  and concentration of the solution, crystals were obtained by slow evaporation at room temperature.

A general overview of these experimental procedures, which also shows the stoichiometries of the investigated salts, is presented in Table 1.

**Table 1** Summary of the synthetic procedures and the stoichiometries of the prepared compounds  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$



The compound of diprotonated ethylenediamine,  $(C_2H_{10}N_2)[VO(C_3H_2O_4)_2] \cdot H_2O$ , was also prepared by reaction of the ammonium salt with ethylenediamine chlorhydrate in aqueous solution [7].

#### *Spectroscopic measurements*

The infrared spectra were recorded with a Perkin-Elmer 580 B spectrophotometer using the KBr pellet technique. Spectra of Nujol-mull-suspensions gave identical results.

#### *TG and DTA studies*

These were carried out simultaneously on a Rigaku thermoanalyzer (type YLDG/CN 8002 L2), using Chromel/Alumel thermoelements. The measurements were performed under a constant  $N_2$  stream (0.4 l/min). The heating rate was 10 deg/min; the maximum heating temperature was 700 °C. Sample weight ranged between 10 and 20 mg and  $\alpha-Al_2O_3$  was used as a DTA standard. Pyrolysis experiments were also carried out, with greater sample amounts, in crucible furnaces in air.

### **Results and discussion**

#### *Infrared spectra*

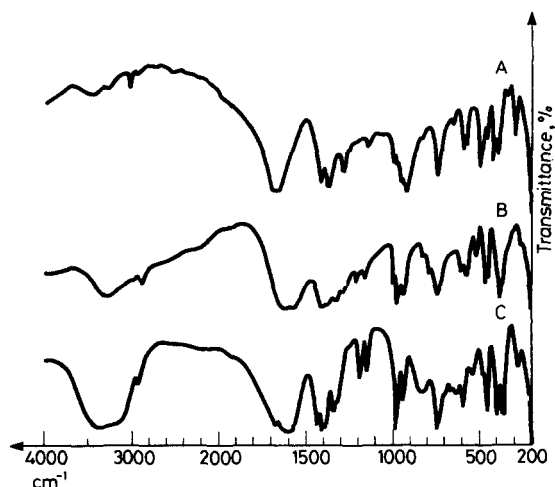
The structure of the bis(malonato)oxovanadate(IV) complex anion is not known with certainty. But, there are two possible structural models. In both, the vanadium atom is coordinated to six oxygen-atoms forming a distorted octahedron. The two pairs of chelated malonato O-atoms can form a *cis*-arrangement with one of the atoms occupying an apical position. The other apical site is taken by the vanadyl O-atom and the remaining equatorial position by a water O-atom. Such type of arrangement has been found, for example, in the bis(oxalato)monoquinoxovanadate(IV) anion [15]. The second possibility would be a *trans*-arrangement of the two malonato groups in the basal plane with the water and vanadyl oxygens in the apical positions.

We expect to obtain a definitive insight into this structural problem by means of a complete structural analysis of the ammonium salt,  $(NH_4)_2[VO(C_3H_2O_4)_2] \cdot 3H_2O$  recently started, and a thorough investigation of other of its physicochemical properties [16].

We have registered the IR spectra of all of the prepared salts and made a general band assignment for all of them. This assignment is based on known data for the free acid [17, 18] as well as for different malonato complexes and salts [18].

As typical examples of the measured spectra, Fig. 1 shows those corresponding to the respective barium, rubidium and thallium salts.

The proposed assignments are shown in Table 2. Some comments about these results are of real interest and deserves further consideration.



**Fig. 1** Infrared spectra of powdered samples of  $\text{Rb}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]$  (A),  $\text{Ba}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  (B) and  $\text{Tl}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  (C)

— Despite some differences in position, resolution and intensity a series of well defined and characteristic spectral ranges are evident in all compounds:

a) OH and CH vibrations are located above  $2900 \text{ cm}^{-1}$ . In the case of the most hydrated salts the main band, at  $3200\text{--}3500 \text{ cm}^{-1}$ , is usually very strong and broad. Not only in the anhydrous rubidium and cesium salts but also in the silver compound, this band is weak, strongly broadened and undefined.

b) Band groups at  $1600$  and  $1400 \text{ cm}^{-1}$  are assigned to the antisymmetric and symmetric (OCO) stretching vibrations, respectively. Also the  $\delta(\text{H}_2\text{O})$  mode is located in the first region and appears strongly overlapped with the carboxylate band. In the second region a similar overlapping occurs with the  $(\text{CH}_2)$ -bending mode.

c) As a consequence of the coordination of the malonate groups to the  $\text{VO}^{2+}$  moiety, the two mentioned carboxylate bands are shifted together, when compared with the value found in the free acid.

d) The  $\text{CH}_2$ -wagging and rocking modes lie near  $1300$  and  $950 \text{ cm}^{-1}$ , respectively. The last band is partially superimposed with the (C—C) symmetric stretching mode. The corresponding (C—C) antisymmetric vibration is found between  $1100\text{--}1200 \text{ cm}^{-1}$ .

e) The appearance of a generally weak band at around  $830\text{ cm}^{-1}$ , which can be assigned to a rocking mode of coordinated water [19], indicates the union of this ligand with the metallic center.

f) In the spectral range below  $700\text{ cm}^{-1}$  the assignments are more difficult, although in this low energy region all the substances show very similar spectral patterns.

g) The  $\nu(\text{VO})$  stretching band lies, in every case, in the typical region for this mode [1, 2, 20]. The band is generally strong and very well defined although in some cases it is partially overlapped by the next group of bands. For this reason there is some uncertainty about its assignment in these few cases (see below). Interestingly, all the measured values lie somewhat lower than that obtained for vanadyl-malonate,  $\text{VO}[\text{C}_2\text{H}_3\text{O}_4] \cdot 2\text{H}_2\text{O}$ , in which it is found at  $1000\text{ cm}^{-1}$  [20].

— The spectra of the calcium, strontium, barium and lead salts are very similar in all the commented typical ranges, suggesting the possibility that, at least the pentahydrates, could be isostructural. Also the rubidium and cesium compounds show very similar spectra, suggesting a possible structural relationship. Interestingly, the spectra of the sodium and potassium salts are somewhat different. But, the spectrum of the potassium compound is particularly undefined and presents, in general, very broad and not well resolved bands.

— The spectrum of the silver salt is not well defined either, it was observed as a Nujol mull between  $\text{AgCl}$  plates in order to avoid possible reactions with the  $\text{KBr}$  matrix and its quality was not very good.

— In the case of the rubidium, cesium and thallium salts the  $\nu(\text{VO})$  band is partially overlapped by the bands of the next region ( $\nu(\text{CC})_s$  and  $(\text{CH}_2)$ -rocking modes). For this reason a precise assignment becomes very difficult. In the case of  $\text{Ag}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  a triplet of bands ( $993, 968$  and  $949\text{ cm}^{-1}$ ) of nearly equal intensity is found in this region, producing also some difficulties in the assignments.

— The observed frequency shifts of the  $\nu(\text{VO})$  bands by changing the counteraction of the complex anion, can be related with properties of the different cations. For example, it is evident that the band position is displaced to lower frequencies in the series  $\text{Ca} > \text{Sr} > \text{Ba} > \text{Pb}$ , following a similar trend often observed in simple inorganic salts of these cations [21, 22] and attributable to an increase in effective nuclear charge in the same direction. A similar trend can be observed in the series of alkaline cation salts; but in this case it is not so important due to the great differences in the individual spectral patterns and also in the stoichiometry of the compounds. In the ammonium salt, this  $\nu(\text{VO})$  band lies at  $988\text{ cm}^{-1}$  [20], i.e. somewhat higher than for the other monovalent cations measured here.

— The assignment of the  $\nu(\text{V—O})$  stretching bands is not easy, although we suggest that the strong doublet located at ca.  $400\text{--}370\text{ cm}^{-1}$  can be ascribed to this

**Table 2** General assignment of the infrared spectra of the investigated compounds (values in  $\text{cm}^{-1}$ ). (Only the counteractions of the complex anion are indicated, for detailed stoichiometries, cf. Table 1)

Ca	Sr	Ba	Pb	Na	K	Rb	Cs	Tl	Ag	Assignments
3480 vs	3500 vs	3440 sh	3480 sh		~3350 vs,br	~3400 w,br	~3300 w,br	~3210 vs,br	~3260 w,br	$\nu(\text{H}_2\text{O}) +$ $\nu(\text{CH})$
3440 sh	3420 sh	3350 vs 3200 sh	3280 vs	3388 vs - 3017 w						
2920 w	2925 m	2935 vw	2905 w	2916 w	2925 w	3000 w	3010 m	~2900 vw		$\nu(\text{CH})$
1690 s	1685 m	1658 m	1660 w	1692 w		1670 s	2920 w	1655 sh		$\text{an}(\text{OCO})_{\text{as}} +$ $\delta(\text{HOH})$
1670 vw	1670 vw				~1630 vs,br	1635 sh	1650 vs,br	1600 vs,br	1594 vs,br	
1620 sh			1603 vs	1645 vs					1562 vs,br	
1600 vs	1620 vs	1615 vs	1575 sh	1588 vs					1459 sh	$\nu(\text{COC})_s +$ $\delta(\text{CH}_2)_{\text{bend}}$
1450 s	1440 sh	1440 vs	1415 vs	1420 vs	1420 vs,br	1395 m	1405 vs	1415 vs	1440 s	
1420 s	1420 vs	1410 s				1355 s	1370 vs			
1405 sh	1405 w	1385 m	1397 m	1404 s						
1385 w										
1350 m	1340 m	1360 m			1330 vs	1265 m	1280 m	1320 s,br	1380 s,br	$(\text{CH}_2)_{\text{wagg}}$
1320 m	1320 m	1310 sh	1320 m	1320 s	1225 w		1125 vs	1165 m		
1165 s	1170 s	1180 m	1165 s	1154 m	1210 w		1110 sh	1140 w	1180 m	$\nu(\text{CC})_{\text{as}}$
	1160 s	1105 m			1165 m					
					1150 w	1125 m				
					1115 w					

990 vs	985 vs	980 vs	975 vs	975 vs	970 m	960 (?) m	975 vs	968 (?) s	v(VO)
955 w	960 w					980 m		993 s	
945 m	945 s	945 m	945 m	940 m	945 m	970 m	960 w	949 m	v(CC) <sub>g</sub> + (CH <sub>2</sub> ) <sub>rock</sub> .
				948 s	920 sh	925 vs	940 m		
820 w	820 w	830 w	815 m	841 vw	905 vs				
740 s	740 s	760 s	735 s	735 s	725 s	845 (?)	815 w	830 vw	(H <sub>2</sub> O) <sub>rock</sub> (?)
715 sh	725 w			745 s, br		730 s	735 s	751 s	(OCO) <sub>bend</sub>
						645 w			
625 m	610 sh	625 w	650 w	658 s	635 w		680 m, br		
585 m	585 s	595 m	570 m	590 s		620 vs			
		545 w	555 sh	551 w	575 m	580 vs			
					560 m	567 s			
455 w	475 w	475 sh	465 m	478 m	470 s	475 vs	560 m		
400 s	460 m	450 s	450 w	449 m	440 m	450 vs	475 m		
370 s	395 s	400 s	400 s	397 vs	405 s	410 s	450 m		
315 w	367 s	365 s	380 sh	376 m	380 m	380 s	400 vs		
	320 w		325 w		325 w	325 w	370 s		
	275 m	280 w	280 w	272 m	275 vs	275 vs	280 m		

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad; \*: not measured.

See text

type of vibrations. This doublet was not present in the free acid. On the other hand, in the vanadyl(IV) acetylacetonate such a band was found at  $481\text{ cm}^{-1}$  [23], in vanadyl(IV) acetate at  $442\text{ cm}^{-1}$  [24] and in the oxygen-bounded vanadyl biuret complexes at  $350/370\text{ cm}^{-1}$  [12].

The presence of a close lying doublet, attributed to V—O-stretching modes, can indicate the possible existence of two not equivalent malonato units in the complex, i.e. supporting the model with a *cis*-arrangement of the malonato ligands. But this unique argument is evidently very feeble and the present available spectroscopic data does not allow an unambiguous decision between the two proposed structural models. Evidently, a more detailed spectroscopic study, specially in the region of the metal-ligand vibrations would be necessary to clarify this question completely.

### *Thermal behaviour*

The study of the thermal behaviour of this series of compounds is specially interesting because it gives an excellent opportunity to visualize the effect of the different cations on the degradation of the complex anion.

On the other hand, very little is nowadays known on the thermal behaviour of malonato complexes, except that the thermolysis of such species is usually very complex (cf. for example [25–27]).

The thermal stability, in air, of all the prepared salts was checked qualitatively by Schramm, after its synthesis [7]. In most cases, the formation of the corresponding metal-divanadate was observed.

We have now investigated the thermal degradation in a quantitative way, by simultaneous TG/DTA measurements in a nitrogen atmosphere and subsequent analysis of the IR spectra of pyrolysis residues and intermediates. Semiquantitative results of the decomposition in a normal air atmosphere are also reported.

### **Calcium, strontium and barium salts**

TG and DTA traces recorded in typical experiments on the three compounds are shown in Fig. 2. It is evident that its behaviour is very similar although not completely identical. The detailed analysis of the three thermograms is shown in Table 3.

In the case of  $\text{Ba}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  and  $\text{Sr}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  the five water molecules are given off in two steps: four of them in the first stage and the remaining one at higher temperatures. Such a behaviour is often found in vanadyl compounds, because one of the water molecules, ligated to the  $\text{VO}^{2+}$  moiety, is usually somewhat stronger bonded.



This effect is not clearly visualized in the calcium salt, because all the water is released in the first step and, apparently, the decomposition of the anion begins earlier. But it is also possible, that in the other cases the release of the fifth water molecule occurs simultaneously with the initiation of the degradation of the complex anion. Notwithstanding, the main degradation process, associated with the last DTA-signal, occurs at very similar temperatures in all cases.

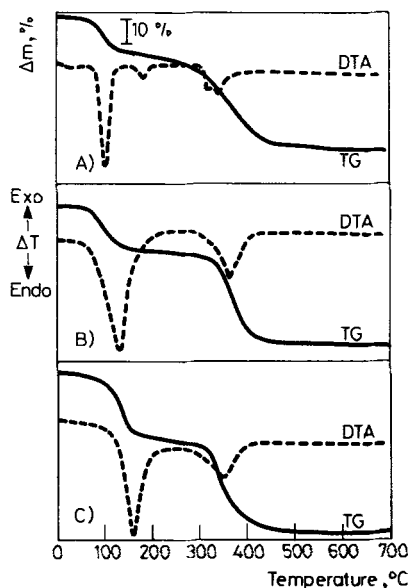
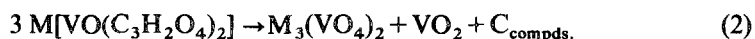


Fig. 2 Typical TG and DTA plots of  $\text{Ba}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  (A),  $\text{Sr}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  (B) and  $\text{Ca}[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$  (C)

It is not possible to establish which are the organic products liberated during the pyrolysis. From the scarce information available on similar processes,  $\text{CO}_2$  and  $\text{CO}$  may be expected as the main products, but also the liberation of methane, ketene and acetic acid have been postulated [26, 27].

The actual real fact is, that after the release of water, the carbon oxides and the organic products the solid residues remaining in the three cases are the same. They satisfy the following general degradation schema:



The presence of orthovanadates could be clearly confirmed by their characteristic IR spectra [28, 29]. Interestingly, in the case of the strontium and barium

Table 3 Analysis of the thermal curves of the alkaline-earth salts of bis(malonato)oxovanadate(IV)

Compound	Step	Temperature range	% wt. loss	Prod. (% theor.)	DTA-signal
Ba[VO(C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] · 5H <sub>2</sub> O	1	20–120 °C	14.8	4 H <sub>2</sub> O (14.4)	110 °C vs endo
	2	120–260 °C	3.4	1 H <sub>2</sub> O (3.6)	190 °C m endo
	3	260–700 °C	31.7	see text (33.5)	315, 340 °C m endo
Sr[VO(C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] · 5H <sub>2</sub> O	1	20–215 °C	19.6	4 H <sub>2</sub> O (20.1)	135 °C vs endo
	2	215–330 °C	4.3	1 H <sub>2</sub> O (4.0)	— — —
	3	330–700 °C	30.8	see text (33.12)	363 °C s endo
Ca[VO(C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] · 5H <sub>2</sub> O	1	20–180 °C	23.0	5 H <sub>2</sub> O (22.4)	162 °C vs endo
	2	180–320 °C	9.5	see text (41.6)	350 °C m endo
	3	320–700 °C	31.8		

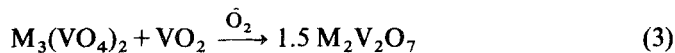
vs: very strong; s; strong; m: medium

compounds, these spectra show the presence of small quantities of the corresponding carbonates ( $\text{SrCO}_3$  and  $\text{BaCO}_3$ ). This fact shows, again, the complexity of the overall degradation process of the organic rest because these carbonates probably resulted from the degradation of some other intermediate carboxylate compounds.

The formation of these carbonates probably explains the small differences observed between the experimental weight losses and those calculated theoretically from Eq. (2) above. In the case of the calcium compound no evidences of the presence of  $\text{CaCO}_3$  could be found from the IR spectra. This fact is probably related with the different thermal stabilities of the alkaline-earth carbonates [30, 31] and/or with a different mechanism at the beginning of the degradation process in the case of the calcium salt, as suggested by the differences in the first step of the pyrolysis.

Taking advantage from the TG/DTA results we have also investigated the decomposition in air of the three alkaline-earth salts, controlling the weight loss and IR spectra at different fixed temperatures. For all the compounds, and at  $500^\circ$ , the formation of the corresponding metal divanadates,  $\text{M}_2\text{V}_2\text{O}_7$ , could be verified, through the measured weight changes and their characteristic IR spectra [32–34].

The intermediate generation of the  $\text{M}_3(\text{VO}_4)_2$  compounds was observed at lower temperatures but, interestingly, neither carbonate nor  $\text{V}_2\text{O}_5$  could be detected. Therefore, in the presence of air, a further reaction can be admitted between the solid products generated according to Eq. (2) above, i.e.:



Theoretical weight changes are in perfect agreement with those found experimentally for the overall decomposition of the three compounds in air. Such changes led to the formation of the corresponding divanadate as the only final solid product.

### Lead salt

The behaviour of the lead compound is very similar to that of the alkaline-earth salts, and its DTA-pattern resembles in a certain way that of the barium salt. Four water molecules are given off in the first TG step, associated with a very strong endothermic DTA-peak at  $110^\circ$  producing a weight loss of 12.4% (theoretical 12.3%). The two remaining water molecules are removed up to  $230^\circ$  (observed weight loss: 6.1%; theoretical: 6.1%) and this process is related to a small endothermic DTA-peak at  $206^\circ$ .

The main decomposition process starts simultaneously with the release of these last two water molecules. A strong and rapid weight loss (28.6%) is observed

between 230 and 315°, associated to a broad and medium intensity endothermic DTA-doublet (272° and 306°). The final solid residue is a 1 : 1 mixture of  $\text{Pb}_3(\text{VO}_4)_2$  and  $\text{VO}_2$ , which formation implies a total weight loss of 46.8% in good agreement with the observed value of 47.2%.

In this case, the treatment of the salt in air also generates very pure  $\text{Pb}_2\text{V}_2\text{O}_7$ , as confirmed by their characteristic IR spectrum [36] and the observed total weight loss.

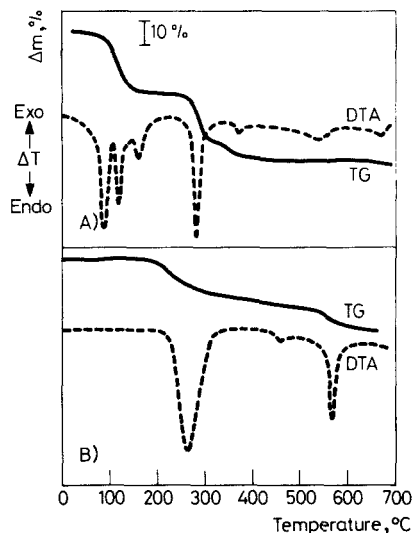


Fig. 3 Typical TG and DTA plots of  $\text{K}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$  (A) and  $\text{Cs}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]$  (B)

### Alkaline salts

The hydrated sodium and potassium salts show similar thermograms, which are different from those of the anhydrous rubidium and cesium compounds. On the other hand, the diagrams of these two last salts are also closely related. As typical examples, the thermal curves of  $\text{K}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$  and  $\text{Cs}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]$  are presented in Fig. 3. The analysis of the experimental data is shown in Table 4.

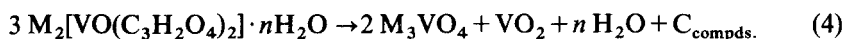
In both, sodium and potassium salts, the release of water occurs at relatively low temperatures and is immediately followed by another, and more important, mass release. In the case of  $\text{K}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$  the release of the first two water molecules can be visualized independently from the other processes and also a low temperature DTA-doublet is observed instead of the unique first peak in the sodium compound.

Table 4 Analysis of the thermal curves of the alkaline salts of bis(malonato)oxovanadate(IV)

Compound	Step	Temperature range	% wt. loss	Prod. (% theor.)	DTA-signal
$\text{Na}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$	1	20–140 °C	12.1	2H <sub>2</sub> O (10.2)	123 vs endo
	2	140–215 °C	5.7		177 s endo
	3	215–330 °C	25.8	SEE TEXT	{ 237 sh endo 254 s endo
	4	330–700 °C	12.9	total wt. loss: 57.4	{ 485 w endo 570 m endo
$\text{K}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$	1	20–110 °C	8.2	2H <sub>2</sub> O (8.5)	90 vs endo
	2	110–165 °C	17.9		{ 120 s endo 165 w endo
	3	165–315 °C	16.2	SEE TEXT	280 vs endo
	4	315–700 °C	13.6	total wt. loss: 56.7	{ 540 w endo 675 w endo
$\text{Rb}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]$	1	20–300 °C	19.8		267 vs endo
	2	300–520 °C	11.8	total wt. loss: 37.7	—
	3	520–700 °C	6.5		{ 535 vw endo 550 vw endo
$\text{Cs}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]$	1	20–275 °C	12.4		264 vs endo
	2	275–540 °C	9.0	total wt. loss: 31.1	460 w endo
	3	540–700 °C	8.5		570 s endo

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder

The spectroscopic analysis of the residues of both compounds show the presence of the corresponding orthovanadate [37] and  $\text{VO}_2$  as final products. This implies the following degradation schema:



The total mass releases observed in both cases support this proposal. For the potassium salt, the theoretical weight loss, according to Eq. (4), would be 56.7% (found: 55.9%) and for the sodium salt the theoretical value is 57.4% (found: 56.5%).

The decomposition of the two higher weight alkaline-compounds is apparently much simpler, as shown in Fig. 3B. They occur through three well defined and continuous steps. The final products are the same as those indicated by Eq. (4), and confirmed also by the total weight losses: for the cesium salt the theoretical weight loss is 31% (found: 29.9%) and for the rubidium compound, theoretical: 37.4% (found: 38.1%).

Apparently, the main decomposition process is initiated at higher temperatures in the two anhydrous compounds, in comparison with the hydrated ones.

It was very difficult to make a quantitative study of the degradation in air, of these four compounds. Incorporation of  $\text{CO}_2$  to the pyrolysis residues, easily detected as carbonate in the IR spectra, takes place during the heating. The alkaline-vanadates, which are also highly hygroscopic, strongly adsorb atmospheric water during their generation, and cause difficulties during the mass and spectroscopic controls (cf. also [38]). Notwithstanding, the IR spectra of the final products show, in all cases, the generation of  $\text{M}_4\text{V}_2\text{O}_7$  as the principal product.

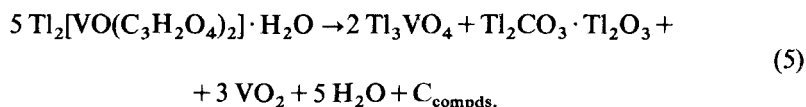
### Thallium and silver salts

These two compounds show a more complex behaviour than the previously discussed salts.

The thermogram of  $\text{Tl}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  show in Fig. 4A is very simple but there are some difficulties for its interpretation. The thermal degradation occurs practically in one single TG step, although some irregularities are seen in the curve. The process is associated with three main endothermic peaks (162, 175 and 192°), one weak shoulder (185°) and a fifth, not well defined and broad endothermic signal at ca. 240°.

The IR spectrum of the solid residues collected at 700° shows not only the presence of  $\text{Tl}_3\text{VO}_4$  [39] and probably  $\text{VO}_2$ , but also some other strong bands characteristic of the carbonato group.

These findings are compatible with the following decomposition schema:



The generation of the basic carbonate, occurs probably through the intermediate formation of  $\text{Tl}_2\text{CO}_3$  which, as it is known [31], decomposes to  $\text{Tl}_2\text{CO}_3 \cdot \text{Tl}_2\text{O}_3$  at  $372^\circ$  with liberation of  $\text{CO}_2$ . The basic compound is stable up to  $615^\circ$  [31]. The slow mass loss observed at higher temperatures in Fig. 4A is probably related with the degradation of this phase.

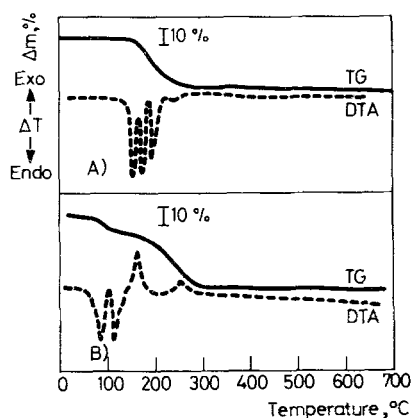


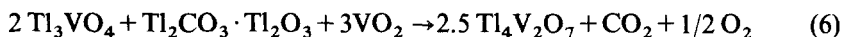
Fig. 4 Typical TG and DTA plots of  $\text{Tl}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  (A) and  $\text{Ag}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  (B)

The process represented by Eq. (5) implies a total weight loss of 24.6%. This figure is in good agreement with the experimental value of ca. 25.0% registered at  $300^\circ$ . The total weight loss, measured at  $700^\circ$  lies around 30%, and suggests the posterior degradation of part of the basic carbonate.

The interruption of the thermal treatment in  $\text{N}_2$ -atmosphere at lower temperatures demonstrates also the complexity of this process because in some intermediate stages the presence of  $\text{Tl}_2\text{V}_6\text{O}_{16}$  [40] alone or together with other thallium vanadates is suggested by the IR spectra. This behaviour is also in good agreement with the known complexity of the  $\text{V}_2\text{O}_5/\text{Tl}_2\text{O}$  system [41].

On the other hand, a not well defined IR spectrum of a product obtained by pyrolysis in air at  $340^\circ$ , suggests also in this case, the formation of  $\text{Tl}_4\text{V}_2\text{O}_7$  [39]. The generation of this last compound is also supported by the observed weight loss of 26.5% which is in excellent agreement with the theoretical value of 26%. The

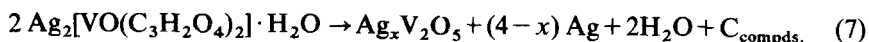
formation of the divanadate can be obviously, explained by the reaction of the solids generated according to Eq. (5), in the presence of air, i.e.:



Also the  $\text{Ag}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  shows a very complex thermal behaviour as can be seen from Fig. 4B. In this case the degradation process occurs in three successive steps, but the analysis of the thermogram is not easy.

Apparently, the first process, related to the strong endothermic DTA-peak located at  $90^\circ$  with a weight loss of 3.6% corresponds to the liberation of the water molecule (theoretical loss = 3.6%). After this step a series of complex events take place (DTA signals at  $118^\circ$  (endo),  $125^\circ$  (endo),  $165^\circ$  (endo)). The last stage, beginning at around  $220^\circ$ , is associated with the last broad endothermic DTA-peak at  $265^\circ$ .

The total mass loss is always approximately of 40%. The IR spectrum of the pyrolysis residues is totally undefined and shows only two very weaks at around  $960$  and  $910 \text{ cm}^{-1}$ , which are characteristic of the so called "vanadium bronzes" [42]. These results are compatible with the following decomposition schema: pyrolysis residues it totally undefined and shows only two very weak bands at around  $960$  and  $910 \text{ cm}^{-1}$ , which are characteristic of the so called "vanadium bronzes" [42]. These results are compatible with the following decomposition schema:



The formation of the "bronze"/Ag-mixture of residues according to this equation would require a weight loss of 39.2%.

On the other hand, the formation of phases of composition  $\text{Ag}_2\text{V}_4\text{O}_{11}$  or  $\text{Ag}_2\text{V}_4\text{O}_{11-y}$  [42, 43] can not be excluded in this system. But, their formation would not affect the overall proposed stoichiometry.

"Vanadium bronzes" are known as very stable phases [42, 43] in inert atmospheres and therefore, their generation in this case is not completely unexpected and is totally acceptable. Also, the presence of metallic silver could be clearly confirmed.

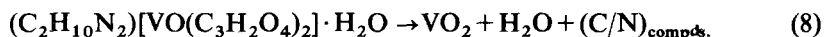
The study of this degradation process in air, was not useful to gain a deeper insight into the characteristics of the thermolysis of this silver salt because it is very difficult to reproduce.

### Diprotonated-enthylenediamine salt

In order to investigate the behaviour of the complex anion in the absence of metallic cations, we have studied the pyrolysis of  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ .



The degradation of this compound occurs practically in one single step. It begins at ca. 160° and extends up to 560° with a total weight loss of 76.1%. Also only one, very strong and broad, endothermic DTA-signal at 215° is seen. The process can be described by the following equation:



for which a weight loss of 76.3% is expected in very good agreement with the experimentally observed value. In air, the pyrolysis conducts to  $V_2O_5$ , as the only final solid residue.

It is interesting to comment that the pyrolysis of the vanadyl(IV) malonate,  $VO(C_3H_2O_4) \cdot 4H_2O$ , occurs in a similar way [44], but the decomposition of the intermediate  $VO(C_3H_2O_4) \cdot 2H_2O$  is associated with an exothermic DTA-peak at 275°, a process during which  $VO_2$  is produced.

\* \* \*

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**Zusammenfassung** — IR-Spektren einer Reihe unhydrierter (Rb, Cs) und hydrierter (Na, K, Ca, Sr, Ba, Pb, Ag, Tl) Salze des komplexen Anions  $[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]^{2-}$  wurden angefertigt und kurz beschrieben. Mittels TG- und DTA-Methoden in Stickstoffatmosphäre, ergänzt durch Untersuchungen in einem Tiegelofen in Luft wurde das thermische Verhalten sowohl obiger Verbindungen als auch des entsprechenden diprotonierten Äthylendiaminkations untersucht. Die Zwischen- und Endprodukte der Pyrolyse wurden mittels IR-Spektroskopie charakterisiert, für die Zersetzungsvorgänge wurden stöchiometrische Betrachtungen angestellt. In den meisten Fällen erhält man als Endprodukt ein Orthovanadat/ $\text{VO}_2$  Gemisch in Stickstoff, in Luft das entsprechende Divanadat.

**Резюме** — Измерены и кратко обсуждены ИК спектры ряда безводных солей (Rb, Cs) и гидратов солей натрия, калия, кальция, стронция, бария, свинца, серебра и таллия со сложным анионом  $[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]^{2-}$ . Термическое поведение этих соединений, также как и соответствующего дипротонированного этилендиамина, было исследовано методами ТГ и ДТА в атмосфере азота и дополнены исследованиями, проведенными в тигельных печах в атмосфере воздуха. Промежуточные и конечные продукты пиролиза были охарактеризованы ИК спектроскопией. Предложена общая стехиометрия процессов дегидратации. В атмосфере азота в большинстве случаев конечными продуктами разложения были смеси ортованадат — двуокись ванадия, тогда как в атмосфере воздуха — получились соответствующие диванадаты.