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Note

THE THERMAL DECOMPOSITION OF CESIUM DIHYDROGEN DECAVANADATE

A.E. LAVAT, E.J. BARAN * and M.E. ESCOBAR

Area de Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900-La Plata (Argentina)

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As part of a series of studies concerning the physicochemical properties of crystalline decavanadates and related compounds, we have recently investigated the thermal stability and decomposition products of the respective silver [1], rare earths [2] and thallium(I) [3] salts.

The present note is devoted to the investigation of the thermal decomposition of a dihydrogen salt of decavanadic acid of formula $Cs_4H_2V_{10}O_{28} \cdot 5H_2O$. The corresponding neutral salt has been investigated earlier [4], but shows a different thermal behaviour and yields distinct decomposition residues.

EXPERIMENTAL

Single crystals of $Cs_4H_2V_{10}O_{28} \cdot 5\ H_2O$ were obtained as described by Jahr and Preuss [5] by the reaction of decavanadic acid and cesium acetate followed by slow evaporation of the resulting solution. The purity was checked by infrared spectroscopy and X-ray diffraction as well as by standard chemical analysis.

TG and DTA measurements were carried out with an automatic recording Mettler thermoanalyzer (type T2/ES), using a Pt–Pt/Rh thermoelement, at a heating rate of 6°C min^{-1} and working under normal atmosphere. Al_2O_3 was employed as DTA standard and sample amounts around 300 mg were used for each run, working in platinum crucibles. The maximum heating temperature was 600°C.

The infrared spectra were recorded on a Perkin Elmer 457 spectrophotometer using the KBr disc technique. X-Ray powder diagrams were obtained with a Philips PW1010 diffractometer, using Cu-K_α radiation (Ni filter) and NaCl as an external calibration standard.

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* To whom correspondence should be addressed.

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RESULTS AND DISCUSSION

The DTA and TG curves for the investigated compounds are shown in Fig. 1 and the corresponding analyses are summarized in Table 1.

According to these results, the dehydration process takes place in two ill-defined steps associated with the strong endothermic peak around 162°C and the weak shoulder at ca. 189°C. Due to the practically continuous weight loss, which begins at 60°C, it is very difficult to determine the amount of water lost in each step.

The following weight loss region, extended up to at least 234°C, is related to the liberation of an additional water molecule resulting from the "deprotonation" of the polyanion. This process is followed immediately by the total decomposition of the polyanion and the exothermic peak located at 248°C is precisely regarded as due to this decomposition. This interpretation is sustained by the fact that the infrared spectra and powder diagrams obtained after this peak show the total absence of bands or diffraction lines related to the original substance.

In order to characterize the decomposition residues and to explain the course of the pyrolisis, pure samples of the compound were heated at selected and well-controlled temperatures (190, 245, 300, 420 and 475°C) in a crucible furnace, according to the information obtained from the thermograms. The residues collected after each heat treatment were allowed to cool in air at room temperature and submitted to infrared and X-ray analysis.

The analysis of the corresponding infrared spectra of the products collected at 190 and 245°C shows that a gradual modification of the structural

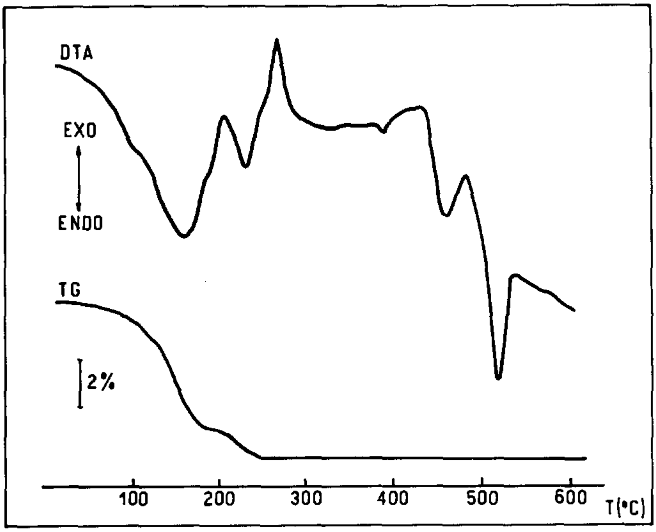

Fig. 1. Typical DTA and TG plots of $Cs_4H_2V_{10}O_{28}\cdot 5\ H_2O$.

TABLE 1

DTA and TG data for $Cs_4H_2V_{10}O_{28} \cdot 5\ H_2O$

T(°C)	Wt. loss (%)	Product (% theor.)	DTA signal
162 189	5.46	5 H_2O (5.69%)	Endo
234	0.93	H_2O (1.13%)	Endo
248		Total decomposition	Exo
389		$Cs_2V_4O_{11}$ cryst. transf.	Endo
469		$Cs_2V_4O_{11}$ fusion	Endo
510		CsV_3O_8 fusion	Endo

characteristics of the polyanion takes place, as it is evident from the observed displacements of the terminal V=O and bridged V–O–V stretching frequencies.

Infrared spectra and X-ray powder diagrams of the fired product collected at 300°C suggest this to be a mixture of $Cs_4V_4O_{11}$ and CsV_3O_8 (cf. refs. 6–8).

The coexistence of these phases in the final product is consistent with the corresponding phase diagram of the V_2O_5/Cs_2O system [6]. According to this diagram, the compound $Cs_2V_4O_{11}$ ($Cs_2O/2V_2O_5$) is dimorphic and presents a crystalline transformation at 380°C. This value is in fair agreement with the endothermic effect observed at 389°C in the thermogram.

The last two endothermic peaks (at 469 and 510°C) can be attributed to the fusion of $Cs_2V_4O_{11}$ and CsV_3O_8, respectively, and these values are also consistent with the melting temperatures reported for these two substances [6].

The results allow the decomposition scheme

$$Cs_4H_2V_{10}O_{28} \cdot 5\ H_2O \rightarrow Cs_4H_2V_{10}O_{28} + 5\ H_2O \qquad (1)$$

$$Cs_4H_2V_{10}O_{28} \rightarrow \text{“}Cs_4V_{10}O_{27}\text{”} + H_2O \qquad (2)$$

$$\text{“}Cs_4V_{10}O_{27}\text{”} \rightarrow Cs_2V_4O_{11} + 2\ CsV_3O_8 \qquad (3)$$

to be formulated.

To support the proposed stoichiometry for the final decomposition products, pure samples of $Cs_2V_4O_{11}$ and CsV_3O_8 were prepared by solid state reactions between appropriate amounts of V_2O_5 and Cs_2CO_3 in a crucible furnace in air. Mixtures of these phases in the proportion indicated above by eqn. (3) were studied by means of infrared spectrometry and X-ray diffractometry. A complete coincidence was achieved between the measurements of these synthetic mixtures and the pyrolysis products of the original decavanadate.

A very slight mass loss was also observed up to the end of the experiment.

This behaviour is characteristic of this type of compound and is due to the formation of non-stoichiometric phases, related to the vanadium bronzes, in which a fraction of vanadium(V) is reduced to vanadium(IV) with the consequent loss of oxygen [4].

Finally, it is interesting to note that this is the first example of a non-neutral decavanadate for which the thermal behaviour is reported. The studied dihydrogen salt shows a different behaviour than the corresponding neutral salt, $Cs_6V_{10}O_{28} \cdot 9\ H_2O$, the pyrolysis of which generates an equimolecular mixture of $Cs_2V_4O_{11}$ and $CsVO_3$ [4].

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