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Note

THE THERMAL DECOMPOSITION OF SILVER DECAVANADATE

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There has recently been renewed interest in the physicochemical properties of crystalline decavanadates. The thermal behaviour of these substances is not yet well understood and it is evident that much more systematic work has to be done in order to clarify this field satisfactorily.

In this note we would like to communicate the results of our investigation of the thermal behaviour of $Ag_6V_{10}O_{28} \cdot 4\ H_2O$, which shows some very interesting aspects and it is also the first decavanadate of a monovalent cation investigated from this point of view.

EXPERIMENTAL

Samples of $Ag_6V_{10}O_{28} \cdot 4\ H_2O$ were prepared according to the method of Jahr and Preuss [1], by reaction of decavanadic acid and silver acetate. Their purity was checked by chemical analysis and their IR spectra [2]. The X-ray powder diagram is also very characteristic, but it is poorly defined [the strongest lines and relative intensities (in parentheses) are: 3.01 Å (100), 2.99 Å (100), 3.28 Å (60), 3.89 Å (55), 2.88 Å (50), 9.03 Å (50)].

Thermogravimetric and differential thermal analyses were carried out on 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 used as DTA standard; sample weight ranged between 250 and 300 mg. For the study of the decomposition residues we used the products obtained by interrupted DTA, or prepared by heating the samples at the stated temperatures in a crucible furnace.

The IR spectra were recorded on a Perkin-Elmer 457 instrument, using Nujol mulls between AgCl plates. X-Ray diffraction powder patterns were obtained on a Philips PW 1010 diffractometer, using Ni-filtered CuK_α radiation.

RESULTS AND DISCUSSION

The analysis of the TG and DTA curves is summarized in Table 1. The four water molecules are lost in two well-defined stages. This behaviour seems to be characteristic for this class of compounds [3,4], pointing to two

TABLE 1

DTA and TG data for $Ag_6V_{10}O_{28} \cdot 4\ H_2O$

T (°C)	% Wt. loss	Product (% theor.)	DTA signal
106	1.79	1.7 H_2O (1.82%)	Endo
175	2.52	2.3 H_2O (2.47%)	Endo
175—276	1.02	0.5 O_2 (0.95%)	Weak endo(?)
274		Total decomposition	Exo
473		Fusion β-$AgVO_3$	Endo
564		Fusion $Ag_2V_4O_{11}$	Endo

types of water molecules in these structures, one of which is more tightly bonded to the cations (cf. also refs. 5 and 6).

Once the dehydration has been accomplished, the TG curve shows a continuous but slow weight loss, which, in practice, ends with the beginning of tje strong exothermic peak located at 274° C.

After this thermal accident, a constant weight region is observed which continuous but slow weight loss, which almost ends with the beginning of the strong exothermic peak located at 274° C.
increment of about 0.35%.

X-Ray and IR spectroscopic analyses of the decomposition residues, as well as comparison with synthetic samples prepared as described below, allow the following decomposition schema to be formulated

$$Ag_6V_{10}O_{28} \cdot 4\ H_2O \rightarrow Ag_6V_{10}O_{28} + 4\ H_2O \quad (1)$$

$$Ag_6V_{10}O_{28} \rightarrow Ag_6V_{10}O_{27} + 0.5\ O_2 \quad (2)$$

$$Ag_6V_{10}O_{27} \rightarrow 2\ \beta\text{-}AgVO_3 + 2\ \text{“}Ag_2V_4O_{10.5}\text{”} \quad (3)$$

$$2\ \text{“}Ag_2V_4O_{10.5}\text{”} + x\ O_2 \rightarrow 2\ Ag_2V_4O_{10.5+x} \quad (4)$$

This implies that after dehydration the anhydrous compound is no longer stable and a small vanadium fraction is reduced with the simultaneous liberation of oxygen [eqn. (2)]. The total decomposition begins at 274° C, according to eqn. (3), with the formation of equimolecular amounts of β-$AgVO_3$ and the non-stoichiometric form of $Ag_2V_4O_{11}$.

The subsequent mass increase can be explained by the uptake of oxygen from this vanadate and the partial re-oxidation of the reduced fraction of vanadium [eqn. (4)]. This behaviour is consistent with the well-known fact that $Ag_2V_4O_{11}$ can exist in the non-stoichiometric form, without appreciable structural modifications [7].

In the recently investigated cases of $Cd_3V_{10}O_{28} \cdot 16\ H_2O$ and $Mg_3V_{10}O_{28} \cdot 18\ H_2O$ the products are mixtures of V_2O_5 and the corresponding “bronzes” and metavanadates [8]. In this last aspect the behaviour of these decavanadates resembles that of the silver compound, because the vanadate $Ag_2V_4O_{11}$ is also closely related to the “bronzes” [7], and is formed together with the corresponding metavanadate.

To support the proposed decomposition schema pure samples of β-$AgVO_3$

and $Ag_2V_4O_{11}$ were prepared by solid-state reactions of appropriate mixtures of V_2O_5 and Ag_2O [7,9]. An equimolecular mixture of both substances shows the same IR spectrum and X-ray powder diagram as the decomposition product.

In this context it is worth commenting that the decomposition products collected immediately after completion of the exothermic peak show a very poor and badly defined X-ray powder diagram, but by heating them for a short period of time at temperatures of about 400° C, very well-defined diagrams can be obtained. This is probably due to the fact that the original product is partially amorphous and is crystallized by the heat treatment.

The last two observed endothermic peaks (473 and 564°C) are also consistent with the proposed schema, because they can be attributed to the fusion of β-$AgVO_3$ and $Ag_2V_4O_{11}$, respectively. The literature values for these processes are 478 and 568° C respectively [9].

The fact that no free V_2O_5 is found in the decomposition products indicates that silver decavanadate has an essentially different behaviour than other decavanadates. In other cases so far investigated [8] or under investigation in our laboratory [6], V_2O_5 is always present in the decomposition residues.

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