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# THE THERMAL DECOMPOSITION OF THALLIUM(I) DECAVANADATE. FIRST EXAMPLE OF A SYMMETRIC PYROLITIC DEPOLYMERIZATION OF THE $V_{10}O_{28}^{6-}$ ANION

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In recent papers we have presented the results of our investigations of the thermal behaviour of silver decavanadate [1] and the rare earth decavanadates [2]. As a continuation of these studies we have now investigated the thermal decomposition of thallous decavanadate and we could observe, for the first time, a symmetric depolymerization of the $V_{10}O_{28}^{6-}$ polyanion as a direct consequence of the thermal treatment.

## EXPERIMENTAL

Samples of $Tl_6V_{10}O_{28} \cdot 6\,H_2O$ were prepared according to the method of Jahr and Preuss [3], by reaction between decavanadic acid and thallous acetate. The deep orange microcrystalline precipitate was filtered, washed with cold water and dried. The purity of the samples was checked by chemical analysis and their IR spectra [4]. It is shown, first by chemical analysis and later by TG measurements, that the samples contain approximately six water molecules instead of the four previously reported for the compound, but prepared in another way [4]. Such discrepancies in the number of water molecules associated with different crystalline decavanadates are not unusual [5], and they are probably due to different drying times and procedures.

Thermogravimetric and differential thermal analyses were carried out on an automatic recording Mettler thermoanalyzer (type T2/ES) using a Pt–Pt/Rh thermoelement and working under normal atmosphere at a heating rate of 6°C $min^{-1}$. $Al_2O_3$ was used as DTA standard; sample weight ranged between 250 and 350 mg.

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The IR spectra were recorded on a Perkin-Elmer 457 instrument, using Nujol mulls between AgCl plates. X-Ray diffraction patterns were obtained on a Philips PW 1010 diffractometer, using Cu$K_\alpha$ radiation (Ni-filter) and NaCl as an external calibration standard.

## RESULTS AND DISCUSSION

Typical TG and DTA diagrams are presented in Fig. 1 and the corresponding analysis of the results is summarized in Table 1. It is seen that the dehydration of the samples occurs in two well-defined stages. The last step extends up to ca. 190°C, after which a small but significant continuous weight loss is observed and it extends, at least, up to 600°C.

In order to allow further characterization of the decomposition residues pure decavanadate samples were heated in a crucible furnace at temperatures of 165, 265, 390, 410 and 500°C, in platinum crucibles in air. IR spectra and X-ray powder diagrams have been recorded for all collected residues. The residues obtained after the first three temperatures show the characteristic powder pattern [6] and IR spectra [7] of thallium(I) pentavanadate, $Tl_3V_5O_{14}$. This result implies firstly, that the decavanadate ion depolymerizes in a symmetric way, and secondly, that this decomposition occurs practically simultaneously with the loss of the remaining water. Therefore, the second observed endothermic peak is a result of the two mentioned processes (i.e. the dehydration and the depolymerization). Consequently, the small exothermic peak located at 202°C is probably due to a structural rearrangement or recrystallization of the generated pentavanadate units, and is not

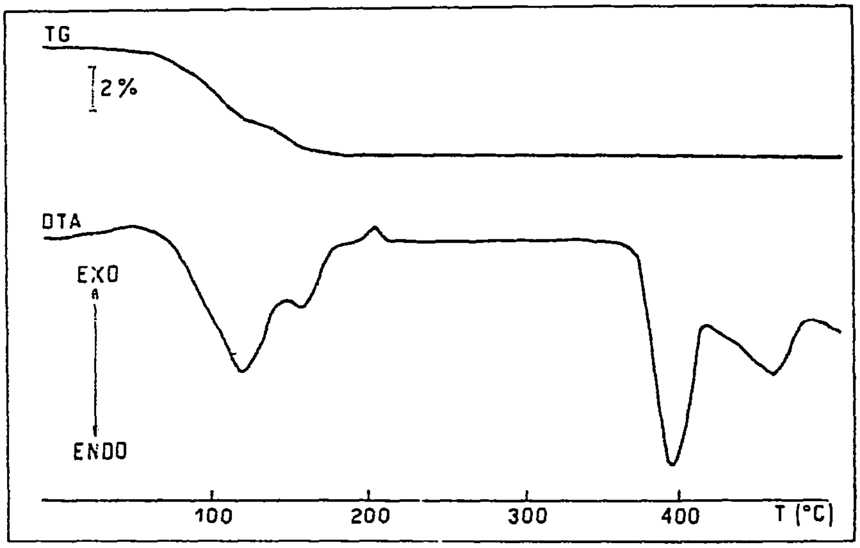

Fig. 1. Typical DTA and TG plots for $Tl_6V_{10}O_{28} \cdot 6\ H_2O$.

TABLE I

Analysis of TG and DTA data for $Tl_6V_{10}O_{28} \cdot 6H_2O$

| $T$ (°C) | % Wt. loss | Product (% theor.) | DTA signal |
|---|---|---|---|
| 120 | 2.67 | 3.4 $H_2O$ (2.67%) | Endo |
| 157 | 2.10 | 2.6 $H_2O$ (2.04%) | Endo |
| 202 | | ? | Exo (weak) |
| 398 | | Fusion $Tl_3V_5O_{14}$ | Endo |
| 461 | | ? | Endo |
| 190–600 | ~0.30 | $O_2$ | None |

related to their formation which, at this temperature, is largely completed.

The strong endothermic peak at 398°C coincides with the fusion of the pyrolysis residue. This is consistent with the literature value of 415°C reported as the melting temperature of the pure pentavanadate [6].

The residues collected after slow cooling of the samples heated at 410 and 500°C show powder diagrams and IR spectra which indicate the presence of a mixture of $TlVO_3$ and $TlV_3O_8$. The formation of these products is also consistent with the known phase diagram of the $Tl_2O/V_2O_5$ system [6].

The fact that practically pure thallium pentavanadate can be recuperated if the fused residues are quenched rapidly in ice-cold water is also interesting. This behaviour is in agreement with results of Zúrková and Miklová [7], who report the formation of $Tl_3V_5O_{14}$ by reaction between $TlVO_3$ and $TlV_3O_8$ at 480°C.

Finally, the origin of the last endothermic peak, observed at 461°C in the DTA curve of Fig. 1 cannot be clearly explained, although it is probably related to a structural change in conformation of the polyanion. The small, continuous weight loss which begins around 190°C is probably related to a loss of oxygen from the generated pentavanadate.

In conclusion, the above results allow the investigated decomposition process to be described as follows

$$Tl_6V_{10}O_{28} \cdot 6\,H_2O \rightarrow Tl_6V_{10}O_{28} + 6\,H_2O \tag{1}$$

$$Tl_6V_{10}O_{28} \rightarrow 2\,Tl_3V_5O_{14} \tag{2}$$

$$(Tl_3V_5O_{14} \rightarrow Tl_3V_5O_{14-x} + x/2\,O_2) \tag{2a}$$

$$2\,Tl_3V_5O_{14} \rightarrow 4\,TlVO_3 + 2\,TlV_3O_8 \tag{3}$$

As discussed above, if the fused product is quenched rapidly, the final product is the pentavanadate, as given by reaction (2) or (2a), but if the residue is slowly cooled a mixture of $TlVO_3$ and $TlV_3O_8$ in a 2:1 molar ratio is obtained according to eqn: (3). It is likely that the $TlV_3O_8$ is also generated in a slightly non-stoichiometric form due to oxygen loss and partial reduction to V(IV) (cf. ref. [7]).

As additional support for the proposed decomposition schema, we have synthesized pure samples of $Tl_3V_5O_{14}$, $TlVO_3$ and $TlV_3O_8$ using known procedures [6]. The IR spectra and powder diagrams of the pentavanadate as well as those of a 2:1 mixture of $TlVO_3$ and $TlV_3O_8$ are completely coincident with those of the residues obtained by thermal treatment according to eqns. (2) and (3).

The results of this study show that the thermal decomposition of $Tl_6V_{10}O_{28} \cdot 6\,H_2O$ under controlled temperature conditions can be useful as a new method for the preparation of very pure $Tl_3V_5O_{14}$ in a very easy and well reproducible way. The purest samples have been obtained interrupting the heating at 250–260°C. It is also interesting that in the presence of thallium(I) as a counter-cation the $V_{10}O_{28}^{6-}$ polyanion is decomposed symmetrically into two equal fragments, and it is also noteworthy that, in the present case, different final decomposition products can be obtained employing different cooling procedures.

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