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Note

THE THERMAL DECOMPOSITION OF VANADYL(IV) HEXACYANOFERRATE(II), $(VO)_2$ $[Fe(CN)_6] \cdot 10H_2O$

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In a recently published paper we have described the preparation and some properties of vanadyl(IV) pentacyanonitrosylferrate(II), $VO[Fe(CN)_5NO] \cdot 2H_2O$ [1]. This compound has shown a very interesting thermal behaviour, which differs markedly from that known for other crystalline pentacyanonitrosylferrates(II) with different cations [2–5].

As we could also obtain very pure samples of the corresponding hexacyanoferrate(II), $(VO)_2[Fe(CN)_6] \cdot 10H_2O$ [1], it is also interesting to investigate the thermal degradation of this complex compound.

EXPERIMENTAL

Pure samples of $(VO)_2[Fe(CN)_6] \cdot 10H_2O$ were prepared as previously described, by a double decomposition reaction between $Li_4[Fe(CN)_6]$ and $VOSO_4$ solutions [1]. They were characterized by chemical analysis and IR and electronic spectroscopies.

Thermogravimetric and differential thermal analyses were carried out simultaneously on a Rigaku thermoanalyser (type (YLDG/CN 8002 L2) using a chromel/alumel thermoelement and working under a constant nitrogen flow (0.4 l min^{-1}). The heating rate was 10°C min^{-1} and Al_2O_3 was used as a DTA standard. The sample weight ranged between 20 and 25 mg and the maximum heating temperature was 700°C.

RESULTS AND DISCUSSION

Typical TG and DTA curves are shown in Fig. 1. The quantitative evaluation of the thermogravimetric curve is presented in Table 1.

It can be observed that in a first step, eight water molecules are lost:

$$(VO)_2[Fe(CN)_6] \cdot 10H_2O \rightarrow (VO)_2[Fe(CN)_6] \cdot 2H_2O + 8H_2O \quad (1)$$

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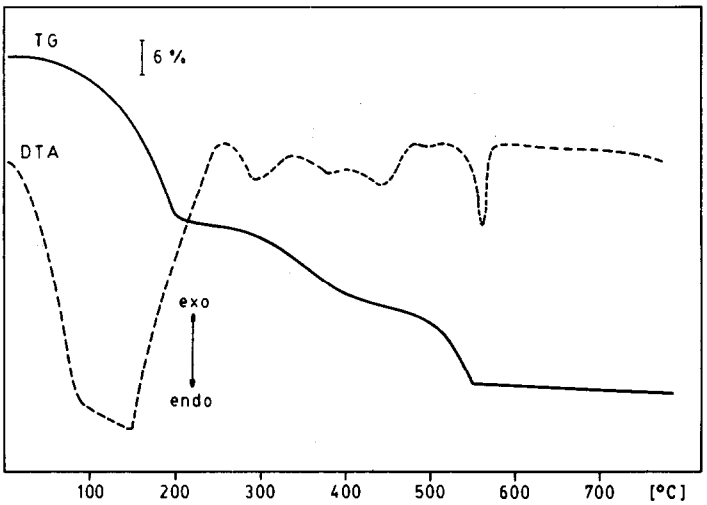

Fig. 1. Typical TG and DTA plots of $(VO)_2[Fe(CN)_6]\cdot 10H_2O$.

The loss of the two remaining water molecules occurs in a very complex way, which involves the evolution of HCN and the generation of VO_2 and "$Fe(CN)_2$"—which should be better formulated as $Fe_2[Fe(CN)_6]$—as solid products:

$$(VO)_2[Fe(CN)_6]\cdot 2H_2O \rightarrow 2VO_2 + \text{"}Fe(CN)_2\text{"} + 4HCN \quad (2)$$

The DTA curve corresponding to this second step shows three broad and not well defined endothermic peaks. This second step reaches 520°C. The last degradation process begins at this temperature. It is associated with the sharp, well-defined DTA peak at 561°C and implies the thermolysis of "$Fe(CN)_2$":

$$\text{"}Fe(CN)_2\text{"} \rightarrow Fe + (CN)_2 \quad (3)$$

According to these results, the following overall decomposition scheme

TABLE 1

Analysis of the thermal data of $(VO)_2[Fe(CN)_6]\cdot 10H_2O$

T (°C)	Wt. loss (%)	Products (% theor.)		DTA signal
~ 86 (sh)	27.5	$8H_2O$	(27.4)	endo
150				endo
297				endo
381	20.5	4HCN	(20.5)	endo
441				endo
561	10.1	$(CN)_2$	(9.9)	endo

can be formulated:

$$(VO)_2[Fe(CN)_6] \cdot 10H_2O \rightarrow 2VO_2 + Fe + 4HCN + (CN)_2 + 8H_2O \quad (4)$$

This scheme suggests the presence of two water molecules, which being more tightly bound, are decomposed in the second degradation step with the release of HCN in a similar way as observed during the thermal decomposition of $VO[Fe(CN)_5NO] \cdot 2H_2O$ [1]. These two water molecules are surely bound directly to the two VO^{2+} cations, probably in *trans*-position to the V=O bond.

A remarkable fact of the investigated process is the final degradation step in which, together with the cyanogen evolution, elemental iron is produced. The generation of $(CN)_2$ at higher temperatures, has often been observed in the case of Fe(II) cyano-complexes [2,3] but, according to a proposal made by Seifer [6], the formation of Fe_3C as the final solid residue is normally postulated. Notwithstanding, in the present case the generation of elemental iron is unambiguously supported by a great number of measurements of different $(VO)_2[Fe(CN)_6] \cdot 10H_2O$ samples. A catalytic action of the previously generated VO_2 might be possible in this last degradation step.

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