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Note

THE THERMAL DECOMPOSITION OF $Na_6[H_2V_2I_2O_{16}] \cdot 10\ H_2O$

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As part of our studies dealing with the spectroscopic and thermal properties of polyoxoanions, we have now investigated the thermal degradation of $Na_6[H_2V_2I_2O_{16}] \cdot 10\ H_2O$. This investigation seems particularly interesting due to the possible generation of I_2 as a pyrolysis product, with or without the intermediate production of I_2O_5. As only a very limited number of examples in which I_2O_5 is generated during a thermal decomposition are already known [1,2], the present study should be useful to extend our knowledge on this type of processes.

EXPERIMENTAL

Pure samples of $Na_6[H_2V_2I_2O_{16}] \cdot 10\ H_2O$ were obtained from V_2O_5, $NaHCO_3$ and H_5IO_6 mixtures according to the procedure described by Mattes and Richter [3]. They were characterized by means of X-ray diffraction and IR spectroscopy [3].

Thermogravimetry and differential thermal analyses were carried out on an automatic recording Mettler thermoanalyser (type TA1) 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 a DTA standard; sample weight ranged between 20 and 30 mg.

The temperature range up to 550°C was scanned by means of a Mettler TA-3000 DSC system in order to obtain more accurate values for the temperature maxima and to get direct information on the enthalpy changes associated with each of the detected processes.

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Taking advantage of the TG, DTA and DSC data obtained, samples were also heated in a crucible furnace in air, for different periods of time and at constant selected temperatures. The partially or totally degraded materials were then submitted to X-ray and IR spectral analyses.

IR spectra were recorded with a Perkin-Elmer 580 B spectrophotometer, using the KBr pellet technique. X-ray powder diagrams were obtained with a Rigaku "Miniflex" CN 2005 diffractometer.

RESULTS AND DISCUSSION

Typical TG and DSC curves are shown in Fig. 1; the information above 550°C is complemented by the corresponding DTA trace. The quantitative evaluation of these curves, together with the Δ*H* values determined are presented in Table 1.

It can be seen that the ten water molecules are lost in three successive steps, involving the release of seven, two and one molecules, respectively. Notwithstanding, the DTA and DSC measurements show that even the release of the first seven molecules involves at least three somewhat differentiated stages. The loss of intramolecular water, associated with the sharp 384°C endothermic peak, takes place immediately after the total dehydration, followed forthwith by the main decomposition process of the polyoxoanion. This final process involves the release of I_2 and O_2 and the generation of Na_3VO_4 as the final solid decomposition residue.

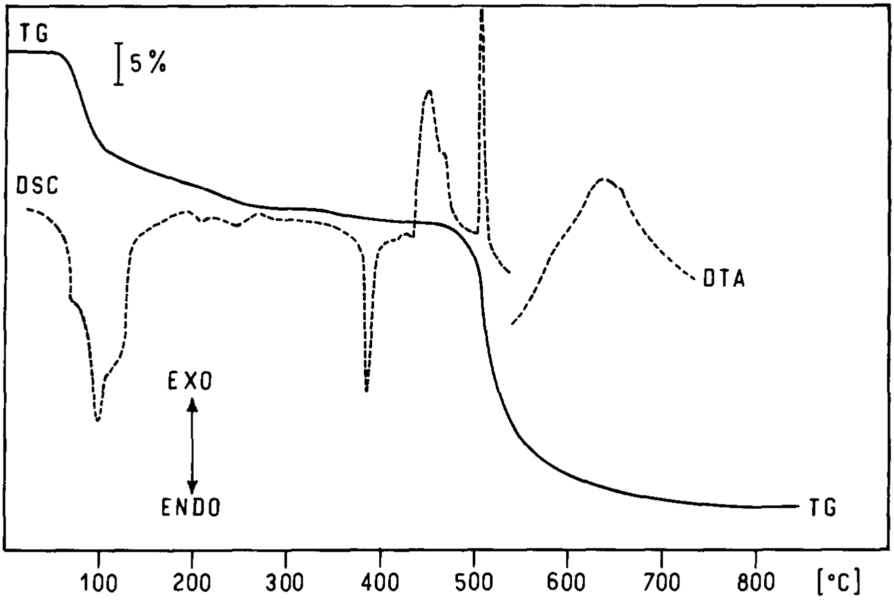

Fig. 1. Typical TG and DSC plots of $Na_6[H_2V_2I_2O_{16}]\cdot 10\ H_2O$.

TABLE 1

Analysis of the thermal data of $Na_6[H_2V_2I_2O_{16}]\cdot 10\ H_2O$

Step	T (°C)	Wt. loss (%)	Product (%theor.)	DSC signal	ΔH (kJ mol^{-1})
1	70	13.8	$7\ H_2O$ (13.52)	endo	357.9
	100			endo	
	115			endo	
2	207	3.7	$2\ H_2O$ (3.86)	endo	5.6
3	242	1.8	$1\ H_2O$ (1.93)	endo	~ 7.0
4	~384	1.8	$1\ H_2O$ (1.93)	endo	44.0
5	445	37.5	$I_2 + 3.5\ O_2$ (39.3)	*exo*	102.3
	458 (sh)			*exo*	
	510			*exo*	20.3
	640			*exo* (*DTA*)	–

According to these results, the following decomposition scheme can be formulated

$$Na_6[H_2V_2I_2O_{16}]\cdot 10\ H_2O \rightarrow Na_6[H_2V_2I_2O_{16}]\cdot 3\ H_2O + 7\ H_2O \tag{1}$$

$$Na_6[H_2V_2I_2O_{16}]\cdot 3\ H_2O \rightarrow Na_6[H_2V_2I_2O_{16}]\cdot H_2O + 2\ H_2O \tag{2}$$

$$Na_6[H_2V_2I_2O_{16}]\cdot H_2O \rightarrow Na_6[H_2V_2I_2O_{16}] + H_2O \tag{3}$$

$$Na_6[H_2V_2I_2O_{16}] \rightarrow \text{“}Na_6[V_2I_2O_{15}]\text{”} + H_2O \tag{4}$$

$$\text{“}Na_6[V_2I_2O_{15}]\text{”} \rightarrow I_2 + 3.5\ O_2 + 2\ Na_3VO_4 \tag{5}$$

The final decomposition (eqn. 5) probably begins immediately after the loss of the intramolecular water, or after the formation of a short-lived intermediate formulated as "$Na_6[V_2I_2O_{15}]$" in eqn. (4). On the other hand, and as shown by the DTA and DSC traces as well as by the results of the constant-temperature studies and subsequent spectroscopic analyses, the last step presumably proceeds through a very complex mechanism which involves the formation of some other intermediate species. One of these intermediates is probably $Na_4V_2O_7$, generated according to

$$\text{“}Na_6[V_2I_2O_{15}]\text{”} \rightarrow I_2 + 3.5\ O_2 + Na_4V_2O_7 + Na_2O \tag{5a}$$

a reaction which is followed by the transformation of the divanadate to orthovanadate

$$Na_4V_2O_7 + Na_2O \rightarrow 2\ Na_3VO_4 \tag{5b}$$

It is well known that the proposed step (5b) must be a relatively slow process, as has been established by systematic investigations of the V_2O_5/Na_2CO_3 system [4,5]. On the other hand, the reaction products collected between 500 and 600°C are highly hygroscopic and strongly absorb

CO_2. Both, free Na_2O and the alkaline-vanadates show such a behaviour. Correspondingly, the IR spectra of such intermediates always show strong water and carbonate absorption bands and evidence for the simultaneous presence of di- and orthovanadate groups. This behaviour also explains the fact that the total mass loss, recorded during TG measurements as well as in the crucible furnace experiments, was always lower than the theoretically predicted value, due to the strong CO_2 and H_2O incorporation. Notwithstanding, samples heated at temperatures above 800°C show only the characteristic IR spectra of pure Na_3VO_4 [6].

It must also be stated here that spectroscopic analysis of the intermediately collected products is not very straightforward due to the fact that only very broad and poorly defined bands are obtained. Neither is the X-ray analysis very useful, because the intermediates are rather amorphous and, on the other hand, powder diagrams in the Na_2O/V_2O_5 system are, as known [4,5], very complex and difficult to interpret.

The most remarkable finding of this study is surely the great thermal stability of the pentavalent iodine incorporated into the investigated polyoxoanion.

In the case of $KCrIO_6$, free I_2O_5 is generated in the primary degradation step at a temperature around 285°C, whereas its posterior decomposition to I_2 and O_2 occurs at 350°C [1]. A similar behaviour has recently been found for $K_4[H_2I_2S_2O_{14}]$; in this case the intermediate formation of I_2O_5 occurs at 212°C and its following decomposition takes place at 360°C [2]. On the other hand, it is currently assumed that pure I_2O_5 is thermally stable up to about 300°C [7].

All these results point to an exceptionally high stabilization of the iodine–oxygen-polyhedra present in the $[H_2V_2I_2O_{16}]^{6-}$ lattice. At temperatures above 450°C, I(V) is reduced and liberated as elementary iodine, because at this temperature there is no possibility of intermediate I_2O_5 formation.

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