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Note

THE THERMAL DECOMPOSITION OF $K_6[Mo_2I_2O_{16}] \cdot 8H_2O$

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As part of our studies dealing with the spectroscopic and thermal properties of polyoxoanions containing iodine [1,2], we have now investigated the thermal behaviour of $K_6[Mo_2I_2O_{16}] \cdot 8H_2O$.

This polyoxoanion has a very interesting structure, constituted by two MoO_6 and two IO_6 octahedral groups. Both MoO_6 octahedra share one edge and each of these octahedra also shares edges with the two IO_6 groups, generating a very compact and distorted structure [3].

EXPERIMENTAL

Pure samples of the compound were obtained by slow evaporation, in a vacuum desiccator over H_2SO_4 and placed in a refrigerator, from a solution containing 5 g of K_2MoO_4 and 0.60 g of H_5IO_6 in 50 ml of water, and to which a KOH solution was added dropwise up to a colour change of phenolphthaleine [3,4]. Chemical analysis of the samples shows that it corresponds to the formula $K_6[Mo_2I_2O_{16}] \cdot 8H_2O$; i.e., an octahydrate was obtained, rather than the formerly described decahydrate [3]. Notwithstanding, the infrared and Raman spectra of our samples were identical to those published by Mattes et al. [3] for the decahydrate.

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 N_2 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 30 mg and the maximum heating temperature was 700°C.

In order to allow the further characterization of the pyrolysis residues or intermediates, the samples were also heated in a crucible furnace in air for different periods of time and at constant selected temperatures. The partially

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or totally degraded samples were then submitted to infrared spectroscopic analyses. The IR spectra were recorded with a Perkin-Elmer 580 B spectrophotometer using the KBr-pellet technique.

RESULTS AND DISCUSSION

Typical TG and DTA curves are shown in Fig. 1. The well-defined endothermic DTA peak at 162°C with a weak shoulder at 150°C is associated with the release of 5.5 moles of water (experimental weight loss = 9.10%; theoretical = 9.16%) according to:

$$K_6[Mo_2I_2O_{16}] \cdot 8H_2O \rightarrow K_6[Mo_2I_2O_{16}] \cdot 2.5H_2O + 5.5H_2O \qquad (1)$$

After this partial release of water, a slow and continuous mass decrease, with increasing temperature, can be visualized. An exothermic DTA signal is observed at 216°C. It is associated with the rupture of the Mo–O–I bonds of the polyoxoanion, and the generation of molybdate and periodate according to: $[Mo_2I_2O_{16}]^{6-} \rightarrow 2IO_4^- + 2MoO_4^{2-}$, whereas the remaining water molecules are still retained by these degradation products.

As it is known, pure anhydrous KIO_4 decomposes very slowly at temperatures above 264°C, progressively generating KIO_3, which is stable between 350 and 524°C [5]. This implies that the slow mass loss observed between the two well-defined TG steps is mainly associated with the release of O_2, generated by the decomposition of the intermediately produced KIO_4, and part of the remaining water. Therefore, the degradation stage which occurs between the two mentioned steps can be formulated as follows:

$$K_6[Mo_2I_2O_{16}]2.5H_2O \rightarrow 2KIO_3 + 2K_2MoO_4[0.5H_2O] + O_2 + 1.5H_2O \quad (2)$$

The experimentally found weight loss of 5.5% agrees very well with the theoretical value of 5.46% calculated from eqn. (2).

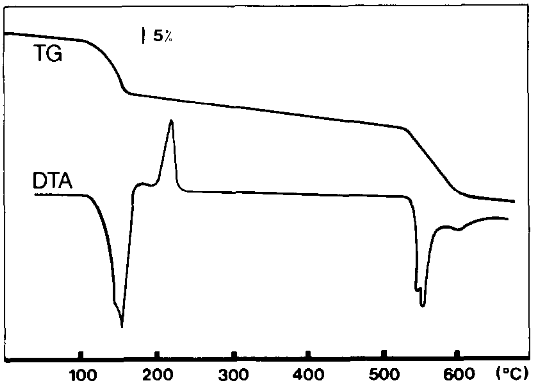

Fig. 1. Typical TG and DTA plots of $K_6[Mo_2I_2O_{16}] \cdot 8H_2O$.

It is specially interesting to notice that the remaining water, indicated as [$0.5H_2O$] in eqn. (2), is strongly retained even at 530°C and is only liberated in the last step of the degradation. It probably remains associated in some way to the molybdate ions immediately after the breakdown of the polyoxoanion.

The IR spectra of samples collected at temperatures around 300°C clearly show the presence of the KIO_4/K_2MoO_4 mixture, whereas those obtained between 450 and 530°C reveal the presence of K_2MoO_4 and KIO_3. The presence of water was definitely established in all these samples. On the other hand, a synthetic 1 : 1 mixture of KIO_3 and K_2MoO_4 gives the same spectral pattern as the residues collected between 450 and 530°C.

Another important mass loss begins at 534°C; it is associated with the endothermic 546–555°C DTA doublet and involves a mass loss of 11%. This mass release can be associated with the above-mentioned residual water and the final decomposition of KIO_3 with the liberation of oxygen:

$$2KIO_3 + 2K_2MoO_4[0.5H_2O] \rightarrow 2K_2MoO_4 + 2KI + 3O_2 + H_2O \qquad (3)$$

The theoretical weight loss, according to this last equation, is 10.55%, in agreement with the experimentally found value.

The IR spectra of totally degraded samples clearly show the presence of K_2MoO_4, whereas the formation of KI could be unambiguously confirmed by some qualitative analytical tests for the iodide ion [6].

Therefore, the overall thermal decomposition of $K_6[Mo_2I_2O_{16}] \cdot 8H_2O$ can be formulated as follows:

$$K_6[Mo_2I_2O_{16}] \cdot 8H_2O \rightarrow 2K_2MoO_4 + 2KI + 8H_2O + 4O_2 \qquad (4)$$

for which a total weight loss of 25.17% is expected in complete agreement with different independent experimental measurements which gave values ranging between 25.4 and 25.8%.

Finally, it must be remarked that the pyrolysis of $K_6[Mo_2I_2O_{16}] \cdot 8H_2O$ is the first example of a new decomposition mechanism for iodine-containing polyoxoanions not previously observed in other compounds of this type. In the cases of $KCrIO_6$ [7] and $K_4[H_2I_2S_2O_{14}]$ [1] I_2O_5 is generated in the primary degradation step and decomposes subsequently into its two components. On the other hand, in the case of $Na_6[H_2V_2I_2O_{16}]$, the degradation is accompanied by the direct liberation of iodine and oxygen [2]. And, finally, in the case just investigated, the iodine remains in the solid pyrolysis residue as KI.

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REFERENCES

1 C.I. Cabello and E.J. Baran, Monatsh. Chem., 116 (1985) 591.
2 E.J. Baran, C.I. Cabello and R.O. Viña, Thermochim. Acta, 90 (1985) 367.
3 R. Mattes, Ch. Matz and E. Sicking, Z. Anorg. Allg. Chem., 435 (1977) 207.
4 R. Mattes, private communication.
5 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.
6 A.I. Vogel, A Textbook of Qualitative Chemical Analysis, 3rd edn., Longmans, Green and Co., London, 1945.
7 A. Kebir and P. Vast, C.R. Acad. Sci., Ser. C, 276 (1973) 503.