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THERMAL BEHAVIOUR OF OXOVANADIUM(IV) COMPLEXES OF HALOGENATED DERIVATIVES OF 8-HYDROXYQUINOLINE

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Abstract

The thermal behaviour of a series of oxovanadium(IV) complexes of halogenated derivatives of 8-hydroxyquinoline was investigated by means of TG and DTA measurements in oxygen atmosphere. V_2O_5 was the final pyrolysis residue in all cases.

Keywords: DTA, halogenated oxines, oxovanadium(IV), TG

Introduction

8-Hydroxyquinoline (oxine) is a well-known analytical reagent which forms stable complexes with a great number of metal cations. However, very little is known about the thermal behaviour of most of them [1–3].

We have recently investigated a number of oxovanadium(IV) and oxovanadium(V) complexes with different oxine derivatives as ligands [4–7]. As a continuation of these studies, we have now investigated the thermal behaviour of some oxovanadium(IV) complexes of halogenated oxines by means of thermogravimetric (TG) and differential thermal analyses (DTA).

Experimental

The following molecules were employed as ligands of the VO^{2+} cation: 5-chloro-, 5,7-dichloro-, 5,7-dibromo-, 5,7-diiodo- and 5-chloro-7-iodo-8-hydroxyquinoline. The schematic structure of these complexes is depicted in Fig. 1 and they were prepared by following the detailed procedures described in a previous paper [5].

TG measurements and DTA were made with a Shimadzu thermoanalytical system (models TG-50 and DTA-50, respectively), in a flowing O_2 atmosphere (50 ml min^{-1}). Experiments were carried out in platinum crucibles at a heating rate

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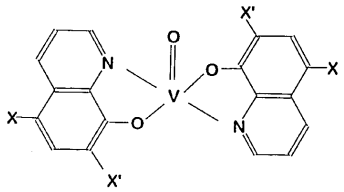

Fig. 1 Schematic structure of the investigated complexes of stoichiometry $VO(X_2Q)_2$

of 10°C min^{-1}. The sample mass ranged between 5 and 10 mg, and Al_2O_3 was used as the DTA standard.

Results and discussion

Three of the obtained TG and DTA traces are shown in Fig. 2. An analysis of the five thermoanalytical curves is presented in Table 1.

Comparisons of the obtained results reveal that the complexes derived from the dichloro- and dibromo-containing ligands exhibit very similar thermal behaviour. Their degradation clearly occurs in two successive steps at practically identical tem-

Table 1 Analysis of the TG and DTA data on the investigated complexes

Complex	V_2O_5 content/%		TG		DTA signals/°C
	found	calcd.	T_{range}/°C	Δm/%	
$VO(Cl_2Q)_2$	18.58	18.45	20–350	22.85	313, w.exo
			350–520	58.57	502, s.exo
					662, v.w.endo
$VO(Br_2Q)_2$	13.56	13.69	20–402	30.21	325, m.exo
			402–530	56.10	490, s.exo
					666, v.w.endo
$VO(I_2Q)_2$	15.10	15.44	20–335	24.70	315, m.exo
			335–510	60.05	345, w.exo; 438, s.exo
					665, v.w.endo
$VO(ClQ)_2$	21.44	21.46	20–360	20.10	290, w.exo
			360–430	9.00	355, v.exo; 428, v.w.exo
			430–500	49.46	483, s.exo
					665, v.w.endo
$VO(ClIQ)_2$	17.81	13.46	20–365	26.90	330, w.exo
			365–450	16.66	374, v.w.exo
			450–550	38.63	482, s.exo
					668, v.w.endo

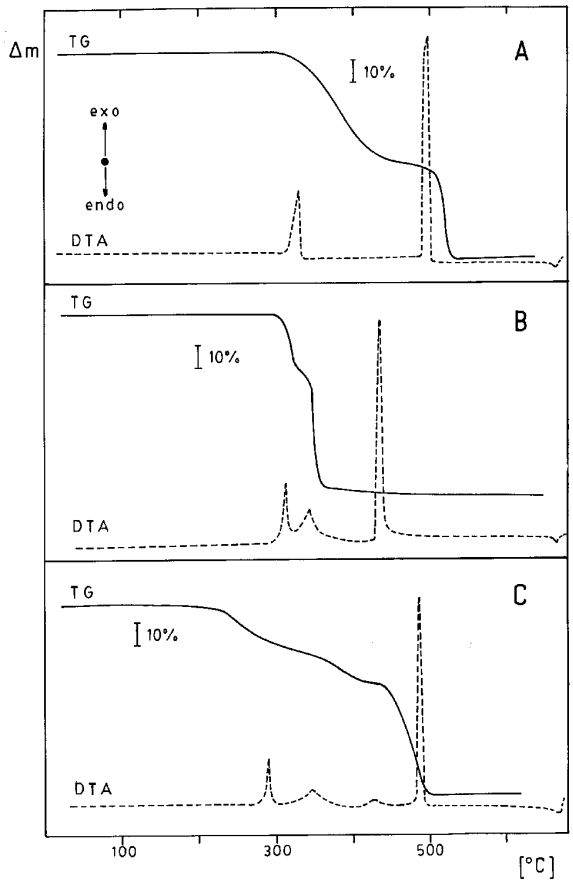

Fig. 2 TG and DTA traces of $VO(Br_2Q)_2$(A), $VO(I_2Q)_2$ (B) and $VO(C1Q)_2$ (C)

peratures. In the case of the diiodo ligand, the two successive steps occur in a narrower temperature range and the final degradation takes place at a somewhat lower temperature than in the other two cases (compare the respective DTA traces of Figs 2A and 2B.

For the other two ligands, the thermal decomposition seems to be somewhat more complex. Three successive TG steps can be identified (cf. Fig. 2C), and the DTA traces display some additional signals.

Although we could not characterize the intermediately generated species, in all cases the final degradation product was V_2O_5, which could be unambiguously identified via IR spectroscopy. The very weak endothermal DTA signal observed in all cases at around 660–670°C, and corresponding to the melting point of V_2O_5 (658°C [8]), also confirms the presence of this oxide.

The calculated pyrolysis residues too agree very well with those found experimentally, as shown in Table 1. Only in the case of the 5-chloro-7-iodo complex does

the experimental value lie appreciably higher than the calculated one. It is possible that a small quantity of iodine may be retained by the residual oxide.

A comparison of our results with those previously reported for some pyridine adducts of the VO^{2+} complex of 5,7-dichloro-8-hydroxyquinoline [9] reveals a good correlation. In the mentioned adducts, the pyridines are lost between 120 and 200°C, generating the dichloro-oxine species, which was found to decompose between 200 and 520°C.

It is interesting that the presence of halogen atoms on the oxine ring does not appreciably affect the thermal stability of the complexes. For the metal complexes of pure 8-hydroxyquinoline, decomposition and oxide formation take place in similar temperature ranges [3].

* * *

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