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Note

THE THERMAL DECOMPOSITION OF $VO[(DMSO)_3SO_4]$

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ABSTRACT

As part of a series of systematic studies on the spectroscopic and thermal properties of complex compounds and simple salts of the vanadyl(IV) cation we have now investigated the thermal degradation of sulphato-tris(dimethylsulfoxide)oxovanadium(IV) ($VO[(CH_3)_2SO]_3SO_4$).

EXPERIMENTAL

Very pure samples of $VO[(CH_3)_2SO]_3SO_4$ were obtained from vanadyl(IV) sulphate and dimethylsulfoxide (DMSO), according to the procedure described by Selbin and Holmes [1]. They were characterized by elemental analysis and IR spectroscopy.

Thermogravimetric and differential thermal analyses were carried out simultaneously on a Rigaku thermoanalyzer (type YLDG/CN 8002 L2) using a Pt/Pt(Rh) thermoelement and working under a constant N_2 flow ($0.4\ l\ min^{-1}$). The heating rate was $5\,°C\ min^{-1}$ and Al_2O_3 was used as a DTA standard. The sample weight ranged between 20 and 25 mg. The maximum heating temperature was 700 ° C.

IR spectra were recorded with a Perkin Elmer 580B spectrophotometer, using the KBr pellet technique.

RESULTS AND DISCUSSION

Conductometric measurements have shown that the complex is a non-electrolyte, indicating that the SO_4^{2-} ion is incorporated as a ligand in the VO^{2+} coordination sphere [1]. This notwithstanding, it is not clear whether the SO_4^{2-} acts as a monodentate or as a bidentate ligand. Owing to strong

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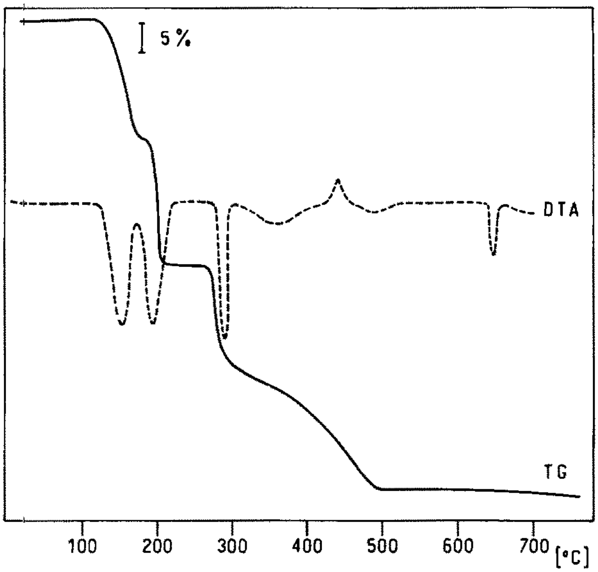

Fig. 1. TG and DTA plots of VO[$(DMSO)_3SO_4$].

overlapping between sulphate and DMSO bands this question cannot be answered using IR spectroscopy. Therefore, the complex could be five or six coordinate, presenting square pyramidal or octahedral geometry.

Typical TG and DTA diagrams are shown in Fig. 1 and the corresponding analysis is summarized in Table 1.

As can be seen, two molecules of DMSO are lost rapidly in two successive steps, associated with the well-defined DTA peaks at 160 and 204°C

$$VO[(DMSO)_3SO_4] \rightarrow VO[(DMSO)_2SO_4] + DMSO \qquad (1)$$

$$VO[(DMSO)_2SO_4] \rightarrow VO[(DMSO)SO_4] + DMSO \qquad (2)$$

The generated intermediate, VO[$(DMSO)SO_4$], which probably possesses a polymeric structure with vanadium in trigonal pyramidal coordination, is

TABLE 1

TG and DTA data for VO[$(DMSO)_3SO_4$]

T (°C)	Wt. loss (%)	Products (% theor.)	DTA (signal)
160	19.6	DMSO (19.65)	endo
204	19.9	DMSO (19.65)	endo
296	19.1	DMSO (19.65)	endo
~ 350	18.0	$SO_2 + \frac{1}{4}O_2$ (18.14)	endo (broad)
~ 440			exo
~ 495			endo
652		Fusion V_2O_5	endo

stable over a more extended temperature range, generating a well-defined plateau between the second and third DTA signals.

The following step seems to be more complex. In fact, from the data of Table 1 it is possible to infer that the third DMSO molecule is lost first, followed immediately by the release of SO_3 and O_2

$$VO[(DMSO)SO_4] \rightarrow VOSO_4 + DMSO \tag{3}$$

$$VOSO_4 \rightarrow \tfrac{1}{2}V_2O_5 + SO_2 + \tfrac{1}{4}O_2 \tag{4}$$

but it is also possible that both processes occur simultaneously, as suggested by the peculiar form of the TG trace.

The generation of V_2O_5 as the only final solid residue is confirmed independently and unambiguously by the characteristic IR spectrum of this oxide [2].

A very remarkable aspect of the last degradation step is the fact that the liberation of SO_2 and O_2 is not accompanied by a well-defined DTA signal. Only the very broad and ill-defined peak at 350 ° C, together with the very weak ones at 440 and 495 ° C, can be observed in this range. In the case of $VOSO_4 \cdot 5H_2O$ the last step, which also corresponds to the degradation of $VOSO_4$ to V_2O_5, SO_2 and O_2, is associated with a very strong and clear endothermic peak at 600 ° C [3].

The different behaviour observed in the present case gives additional support to our suggestion, since processes (3) and (4) may occur simultaneously and may involve, eventually, other intermediates originating from a partial degradation of the last DMSO molecule.

Another interesting aspect of the thermal behaviour of this complex is the above-mentioned high stability of the last intermediate. Its decomposition begins at around 290 ° C even though the boiling point of DMSO lies at 190 ° C [4].

Finally, it should be emphasized that this complex is one of the rare examples in which V_2O_5 can be obtained directly from a vanadyl(IV) species in an inert-gaseous atmosphere. In all the other recently investigated complexes, i.e. a series of bis-malonato vanadyl salts [5], VO(biuret)SO_4 [6], vanadyl formate [7], VO(bipyridine)SO_4 [7], etc., VO_2 is obtained as the final residue in N_2 atmosphere.

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REFERENCES

1 J. Selbin and L.H. Holmes, Jr., J. Inorg. Nucl. Chem., 24 (1962) 1111.
2 L.D. Frederickson and D.M Hausen, Anal. Chem., 35 (1963) 818.
3 M.R. Udupa, Thermochim. Acta, 51 (1981) 169.
4 H.L. Schläfer and W. Schaffernicht, Angew. Chem., 72 (1960) 618.
5 A.L. Rocha and E.J. Baran, J. Thermal Anal., 34 (1988) 693.
6 E.J. Baran, S.B. Etcheverry and D.S.M. Haiek, Polyhedron, 6 (1987) 841.
7 E.J. Baran et al., in preparation.