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THE THERMAL DECOMPOSITION OF SODIUM OXOMOLYBDENUM(VI) OXALATE

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ABSTRACT

A new molybdenum(VI) oxalato complex, $Na_2[Mo_2O_6(C_2O_4)]\cdot 4\ H_2O$ (SMO), with a molybdenum: oxalate ratio of 2 : 1 is prepared and characterised by chemical analysis and IR spectral studies. Thermal decomposition studies were made using TG and DTA techniques. SMO loses its four moles of water in two stages, two moles in each. The first stage extends from 55 to 110°C and the second from 110 to 210°C. Decomposition of the oxalate takes place between 260 and 410°C in a single step to give the end product $Na_2Mo_2O_7$, which was characterised by chemical analysis, IR and X-ray studies. The X-ray diffraction pattern of SMO confirms that it is a crystalline compound.

INTRODUCTION

Molybdenum in the oxidation state (VI) forms a number of oxo compounds, some of which are oxalato complexes. Among the mononuclear complexes $NaNH_4[MoO_3(C_2O_4)]\cdot 2\ H_2O$ [1], (Quin $H)_2[MoO_2(C_2O_4)_2]$ [2] and $A_2[MoO_3(C_2O_4)\cdot H_2O$ [3] ($A = K^+, NH_4^+$) have been prepared and characterised. Binuclear molybdenum(VI) oxalato complexes, e.g. $M_2[Mo_2O_5(C_2O_4)_2(H_2O)_2$ [4,5] ($M = K$, Rb, Cs, NH_4^+) have also been studied. Na, Rb, Cs and ammonium oxodiperoxyoxalato molybdates(VI) [6] have also been prepared and studied.

In all these complexes, the ratio of molybdenum: oxalate is either 1 or < 1. The present paper deals with the preparation and characterisation of the compound $Na_2[Mo_2O_6(C_2O_4)]\cdot 4\ H_2O$ (SMO), with a molybdenum: oxalate ratio of 2 : 1, which has not been observed in any of the above compounds.

EXPERIMENTAL

Baker analysed ammonium para-molybdate and Analar grade sodium oxalate were employed in the preparation of SMO as follows. To a hot

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solution of 1.34 g of sodium oxalate in about 250 ml of water, 2.879 g of MoO_3 (prepared by heating ammonium para-molybdate to about 400°C for 2 h) were added in small lots. The solution was filtered to remove any unreacted MoO_3 and the clear solution was concentrated to about 40 ml to obtain the crystals of SMO. The crystals were washed with a small amount of water and then air-dried in a desiccator.

Molybdenum in the compound was determined gravimetrically as molybdenyl oxinate and oxalate by $KMnO_4$ oxidation. Sodium was estimated by flame photometric method. Analysis of the sample gave: Na^+ 9.27%, Mo 38.79%, $C_2O_4^{2-}$ 17.79%, and H_2O 14.50%, whereas the calculated values for $Na_2[Mo_2O_6(C_2O_4)] \cdot 4\ H_2O$ are: Na^+ 9.31%; Mo 38.85%, $C_2O_4^{2-}$ 17.81, and H_2O 14.57%. These data show that there is no noticeable deviation for SMO with the composition $Na_2[Mo_2O_6(C_2O_4)] \cdot 4\ H_2O$.

Thermogravimetry (TG) was carried out using a Stanton-Redcroft TG 770 thermobalance equipped with a servoscribe automatic recorder, and differential thermal analysis was carried out on a Stanton-Redcroft DTA 673-4. Approximately 5–10 mg samples were taken in platinum crucibles for TG and the heating rate was 10°C min^{-1}. For DTA, 15–20 mg samples were taken in quartz crucibles, using ignited alumina as reference material, and the heating rate was 10°C min^{-1}. Isothermal heating was carried out in a muffle furnace fitted with a pyrometer and temperature controller. IR spectra were recorded on a Beckman IR-20 double beam instrument in the range 250–4000 cm^{-1}, with samples in the form of KBr pellets. The X-ray diffraction patterns were taken on a Philips diffractometer using Cu K_α

TABLE 1

IR and X-ray data on SMO

IR data of SMO			X-Ray data of SMO
Band position (cm^{-1})		Assignment	d values (Å), $\lambda = 1.5405$ Å
3500	S, br	ν(OH) of unco-ordinated water	6.739 [a]
1700	VS		5.711 [b]
1640	S	νas(C=O)	
1605	S		5.196 [b]
1440	W, br	νsym(C–O) + ν(C–C)	3.859 [c]
1360	VS	νsym(C–O) + δ(O–C=O)	3.633 [b]
1305	W		3.558 [c]
935	S	νas Mo=O	3.223 [c]
900	S	νsym Mo=O	3.192 [b]
810	S	ν(O–C=O) + ν(M–O)	3.027 [b]
600	S, br	ν(O–Mo–O)	2.995 [b]
485	W	νsym(O–C–O)	2.877 [c]

S = Strong, VS = very strong, W = weak, br = broad, as = asymmetric, sym = symmetric.

[a] Strongest, [b] very strong, [c] strong.

radiation, and show SMO to be a crystalline compound. Some of the *d* values are given in Table 1.

RESULTS AND DISCUSSION

The results of the IR studies [Fig. 1(A)] of SMO are summarized in Table 1, and the normal bands for the co-ordinated oxalato group have been assigned in accordance with that in other oxalato complexes [7,8]. Besides the fundamental bands due to the co-ordinated oxalato group, the compound shows fairly strong bands at 935, 900 and 600 cm^{-1}. The strong bands at 935 and 900 cm^{-1} suggest the presence of metal–oxygen double bonds [9,10], which have been assigned to asymmetric and symmetric Mo═O stretching, respectively [11]. The broad band at 600 cm^{-1} is similar to one which is observed in the IR spectra of MoO_3, and accordingly may be assigned to the O–Mo–O stretching.

IR spectra of the compound heated to about 300, 340 and 380°C has only the oxalate group bands, indicating that no intermediate carbonate is formed.

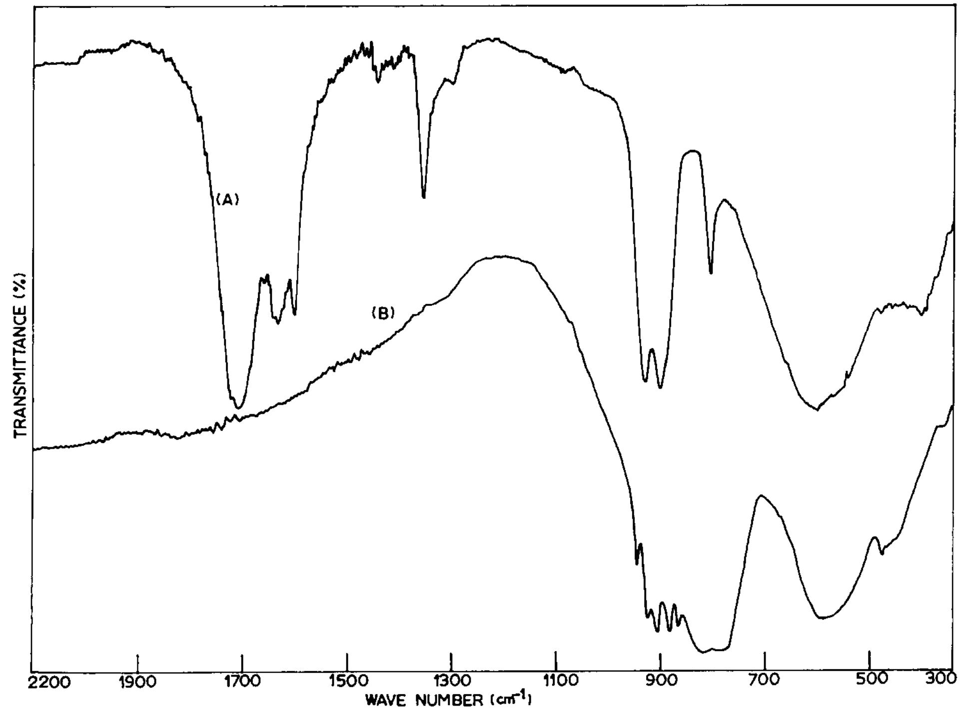

Fig. 1 IR spectra of (A) SMO and (B) SMO heated to 625°C.

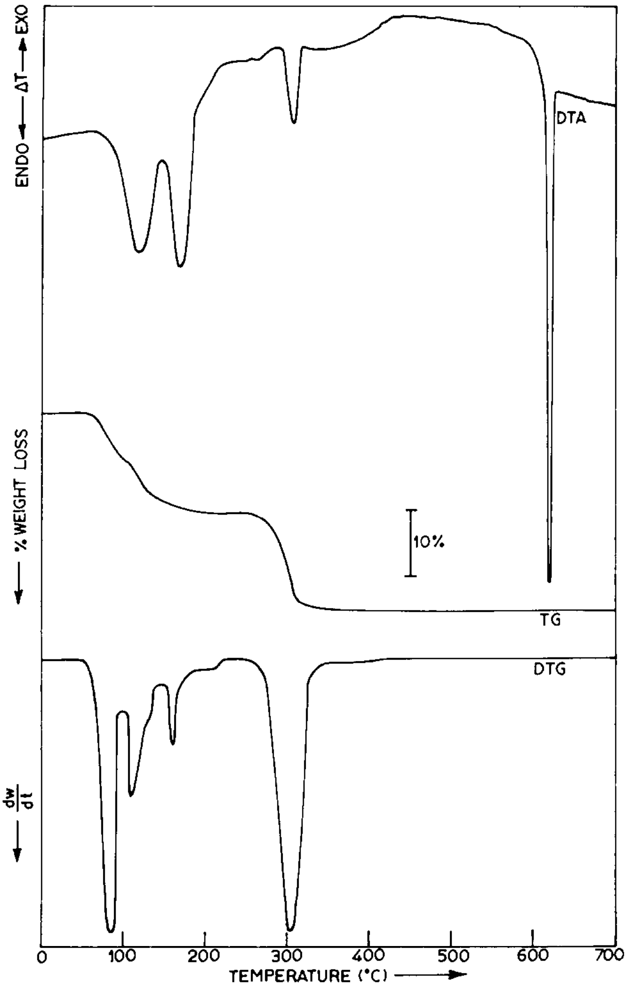

Fig. 2. DTA, TG and DTG curves of SMO in air.

The IR spectra of the compound obtained by heating SMO isothermally to about 430°C and that of the solidified molten product obtained at 625°C are exactly superimposable, and the bands [Fig. 1(B)] closely resemble those reported for $Na_2Mo_2O_7$ [12].

Figure 2 gives the DTA, TG and differential thermogravimetric (DTG) curves for SMO in a static air atmosphere. The thermogram shows that the dehydration takes place in two steps, followed by the decomposition of the anhydrous SMO to give the end product $Na_2Mo_2O_7$. The data on the weight losses are given in Table 2. The various stages are discussed in detail below.

TABLE 2

Analysis of the thermogravimetric curve

Thermal change	Weight loss (%)	
	Obsd.	Calcd.
First step: dehydration	7.52	7.28
Second step: dehydration	7.02	7.29
Decomposition of oxalate	14.52	14.58

Dehydration

As seen from TG (Fig. 2), SMO loses its water in two steps, the first stage extending up to 110°C and the second from 110 to 210°C. However, in DTG the entire process appears to occur in three steps, as three peaks are observed at 85, 110 and 160°C. It appears that SMO first loses one mole of water and before this loss is complete, loss of the second mole of water starts, thus giving the first two peaks. The peak at 160°C may correspond to the loss of the other two moles of water per mole of SMO. The DTA curve indicates that the dehydration takes place in two steps and accordingly two broad endothermic peaks are observed, one at about 115°C and the other at 165°C. The broad peak at 115°C may be due to the combination of two peaks resulting from the loss of the first two moles of water.

The observed weight loss in the first stage is 7.52%, which corresponds to the loss of two moles of water per mole of SMO, the calculated value being 7.28%. The weight loss in the following step corresponds to the loss of the remaining two moles of water. The observed weight loss is 7.02% compared with the calculated value of 7.29%. The difference in observed and calculated values may be attributed to the overlap of part of the two steps.

Decomposition of the oxalate

Decomposition of the oxalate occurs between 260 and 410°C in a single step, as seen on the TG curve. The observed weight loss is 14.52% compared with the calculated value of 14.58%. In DTA, the decomposition of the oxalate is observed as an endothermic peak at about 310°C, and in DTG at about 305°C.

The total observed weight loss for the process

$$Na_2[Mo_2O_6(C_2O_4)] \cdot 4\,H_2O \rightarrow Na_2Mo_2O_7$$

is 29.03% compared with the calculated value of 29.15%.

Melting

An additional endothermic peak is observed in DTA at about 620°C; no corresponding weight change is observed on the TG curve. Thus the peak at 620°C in DTA may be due to some physical change, and it has been attributed to the melting of the end product. On heating isothermally at 625 ± 5°C the sample gives a molten product which immediately solidifies to a white crystalline compound, confirming the peak at 620°C to be due to melting.

The end product was characterised by chemical analysis of the solidified molten product obtained by heating SMO isothermally at 630°C as well as at 430°C. Both these products gave identical chemical analysis, IR and X-ray diffraction patterns. All these studies reveal the formation of pure $Na_2Mo_2O_7$ without any other phase. The observed *d* values closely match with the earlier reported data [13]. A comparision of some of the observed and reported *d* values is given in Table 3.

The above results and discussions based on TG and other data allow a two-stage scheme to be proposed for the thermal decomposition of SMO

$$Na_2[Mo_2O_6(C_2O_4)]\cdot 4\ H_2O \xrightarrow{55-110^{\circ}C} Na_2[Mo_2O_6(C_2O_4)]\cdot 2\ H_2O + 2\ H_2O \tag{1a}$$

$$Na_2[Mo_2O_6(C_2O_4)]\ 2\ H_2O \xrightarrow{110-210^{\circ}C} Na_2[Mo_2O_6(C_2O_4)] + 2\ H_2O \tag{1b}$$

$$Na_2[Mo_2O_6(C_2O_4)] \xrightarrow{260-410^{\circ}C} Na_2Mo_2O_7 + CO + CO_2 \tag{2}$$

TABLE 3

d Values for $Na_2Mo_2O_7$(Å)
$\lambda = 1.5405$ Å

Observed	Reported	Observed	Reported
7.358	7.36	2.90	2.901
5.92	5.92	2.743	2.746
5.489	5.49	2.631	2.635
4.70	4.706	2.597	2.599
4.603	4.609	2.565	2.566
3.77	3.776	2.534	2.534
3.216	3.22	2.517	2.518
3.152	3.153	2.305	2.305
3.124	3.125	2.149	2.149
3.063	3.064	2.128	2.122
2.998	3.00	2.084	2.085
2.954	2.959	2.068	2.069
		1.974	1.975

Equations (1a) and (1b) indicate the two different stages of dehydration and the eqn. (2) represents the decomposition of the oxalate to give the end product.

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