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Note

PYROLYSIS OF STRONTIUM OXOMOLYBDENUM(VI) OXALATE

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The complex $Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ (SMO) was prepared and characterized by chemical analysis and IR spectral studies. Thermal decomposition studies were made by using TG and DTA techniques. The dehydration of SMO takes place in two steps, 105–195 and 195–220 °C, two moles of water being lost in each step. The decomposition of anhydrous SMO occurs between 220 and 360 °C in two steps. The first step extends up to 300 °C to give an intermediate compound with the tentative composition $Sr_3[Mo_6O_{20}(C_2O_4)] \cdot CO_2$ which decomposes in the second step to give the end product. The end product was found to be a mixture of $SrMoO_4$ and MoO_3, as characterized by chemical analysis, IR spectral and X-ray diffraction studies. However, only $SrMoO_4$ was found to exist at 850 °C.

Molybdenum(VI) forms a number of oxalato complexes [1]. A literature survey reveals that only the alkali metal cations have been employed to prepare the molybdenum(VI) oxalato complexes, although a molybdenum(V) oxalato complex with Ba^{2+} as the cation has been prepared and studied [2]. Recently, the thermal decomposition of a new molybdenum(VI) complex, $Ba[MoO_3(C_2O_4)] \cdot 3H_2O$ was also prepared and studied [3]. The present paper deals with the preparation, characterization and thermal decomposition of a new molybdenum(VI) complex, $Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ (SMO).

EXPERIMENTAL

Baker analysed ammonium paramolybdate and AnalaR grade strontium chloride and oxalic acid were used to prepare SMO as follows. To a hot solution of 1.2605 g of oxalic acid in about 200 ml of water, 1.4395 g of MoO_3 (prepared by heating ammonium paramolybdate at about 400 °C for 2 h) were added in small lots. The solution was filtered to remove any unreacted MoO_3 and 1.3331 g of strontium chloride was then added. The solution was concentrated to about 35 ml and allowed to stand for about 15 days to obtain crystals of SMO which were washed with water and dried in a vacuum desiccator.

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Strontium in SMO was determined as sulphate after destroying the oxalate, and molybdenum was determined as molybdenyl oxinate. The oxalate was determined by $KMnO_4$ oxidation. Analysis of the sample gave: Sr^{2+}, 14.45; Mo, 31.55; $C_2O_4^{2-}$, 28.96%, whereas the calculated values for $Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ are: Sr^{2+}, 14.42; Mo, 31.58; $C_2O_4^{2-}$, 28.97%. These data show that there is no noticeable deviation for SMO with the composition $Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$.

Thermogravimetry (TG) was carried out on a Stanton-Redcroft TG 770 thermobalance by taking 5–10 mg samples and a heating rate of 3°C min^{-1}. The DTA was done on a Stanton-Redcroft DTA 673-4 using 15–20 mg samples, and a heating rate of 10°C min^{-1}. Both studies were carried out in an atmosphere of static air. IR spectra were recorded in KBr matrix on a Beckman IR-20 double-beam instrument in the range 250–4000 cm^{-1}. The X-ray diffraction patterns were taken on a Philips diffractometer using CuK_α radiation. The magnetic measurements were performed on a Vibrating Sample Magnetometer model VSM-155 at room temperature (23°C), using a magnetic field of 5500 Gauss.

RESULTS AND DISCUSSION

SMO is a white crystalline compound and is found to be diamagnetic in nature, suggesting that it is a molybdenum(VI) complex. The results of the IR studies of SMO (Fig. 1A) are summarized in Table 1. The normal bands due to the coordinated oxalato group have been assigned on the basis of existing data in the literature [4,5]. The two strong bands at 960 and 920 cm^{-1} suggest the presence of metal–oxygen double bonds and, accordingly, they have been assigned to asymmetric and symmetric Mo=O stretches, while the band at 750 cm^{-1} probably results from an O–Mo–O stretch [6,7]. In addition to these, three weak bands at 900, 770 and 670 cm^{-1} have also been observed which, probably, are due to the rocking, wagging and the metal–oxygen stretching vibrations, respectively, of the coordinated water [8].

Figure 2 gives the DTA, TG and differential thermogravimetric (DTG) curves for SMO in an atmosphere of static air. The thermogram shows that the dehydration of SMO takes place in two steps and it is immediately followed by the decomposition of anhydrous SMO which is also found to be a two-step process. The various stages are discussed in detail below.

Dehydration

As seen from TG, SMO is stable up to 105°C and then loses its water in two stages, the first stage extending up to 195°C and the second from 195 to 220°C. The first stage corresponds to the loss of two moles of water per

TABLE 1

IR absorption bands of SMO and their probable assignments

Frequency (cm^{-1})[a]	Probable assignment[b]
3500 VS,br	ν(OH) of uncoordinated water
1670 VS	ν_{as}(C=O)
1440 S	ν_s(C–O)+ ν(C–C)
1300 S	ν_s(C–O)+ δ(O–C=O)
1285 S	
960 S	ν_{as}(Mo=O)
920 S	ν_s(Mo=O)
900 W	Coordinated water
820 S	ν_s(C–O)+ δ(O–C=O)
790 S	δ(O–C=O)+ ν(M–O)
770 W	Coordinated water
750 M	ν(O–Mo–O)
670 W	Coordinated water
540 M	ν(M–O)+ ν(C–C)
485 M	Ring def. + δ(O–C=O)
400 M	ν(M–O)+ ring def.

[a] VS = very strong; S = strong; M = medium; W = weak; br = broad.

[b] s = symmetric; as = asymmetric; δ = bending.

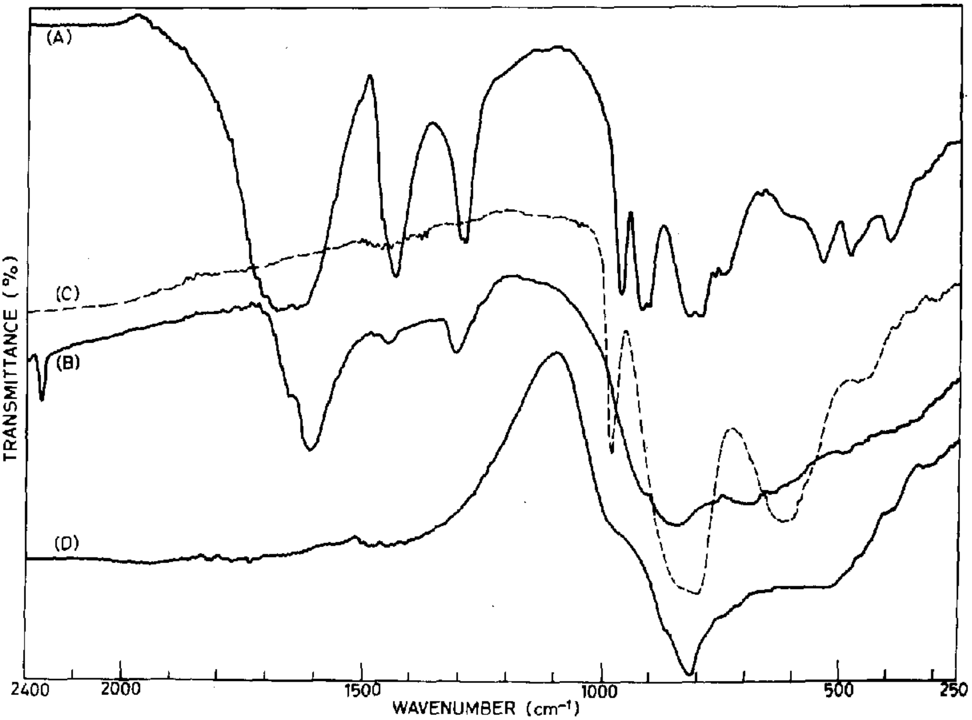

Fig. 1. IR spectra of SMO(A), SMO heated to 305°C (B), SMO heated to 375°C (C) and SMO heated to 850°C (D).

mole of SMO. This is observed in DTA and DTG as peaks at 185 and 190 °C, respectively. The observed weight loss is 5.95% against the calculated value of 5.92%. The second stage corresponds to the loss of the other two moles of water per mole of SMO, both DTA and DTG showing peaks at 215 °C. The observed weight loss is 5.95% while the calculated value is 5.93%. The loss of the latter two moles of water at such a high temperature indicates that they are probably coordinated to the metal.

Decomposition of oxalate

The dehydration of SMO is immediately followed by the decomposition of oxalate which occurs between 220 and 360 °C in two stages. The first

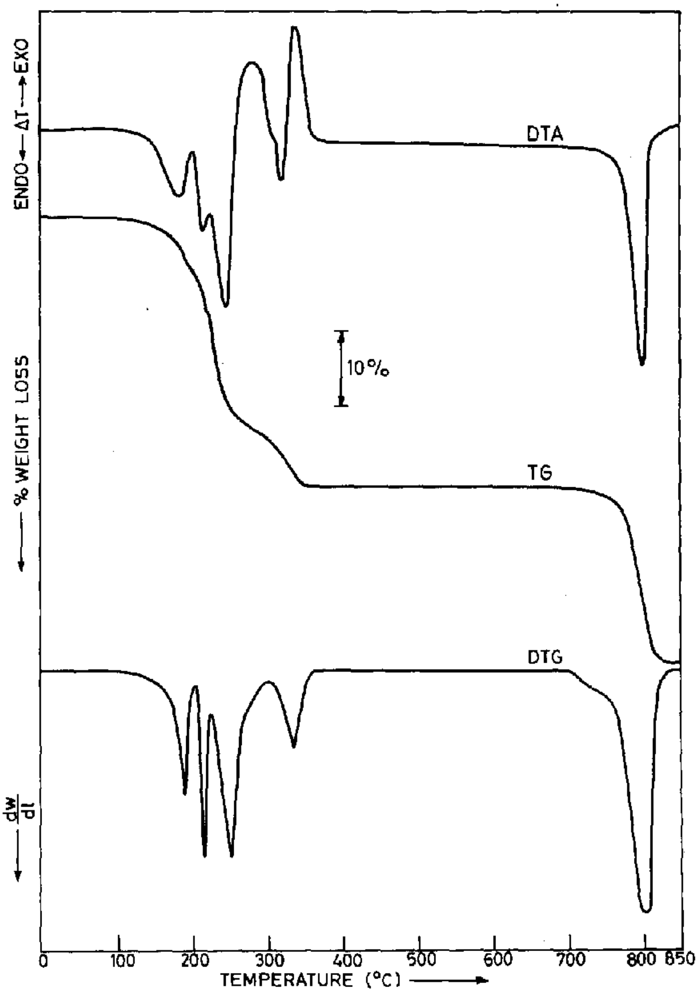

Fig. 2. DTA, TG and DTG of SMO in air.

stage extends up to 300 °C and corresponds to the loss of five moles of carbon monoxide and four moles of carbon dioxide per three moles of anhydrous SMO to give an intermediate compound with the tentative composition $Sr_3[Mo_6O_{20}(C_2O_4)] \cdot CO_2$. This is observed in DTG as a peak at 250 °C. However, in DTA, an endothermic peak at 245 °C is immediately followed by an exothermic peak at 280 °C, which may be due to the domination of oxidation of carbon monoxide into carbon dioxide. The observed weight loss is 17.38% against the calculated value of 17.33%. The second stage occurs between 300 and 360 °C and involves the decomposition of $Sr_3[Mo_6O_{20}(C_2O_4)] \cdot CO_2$ to give the end product which is found to be a mixture of strontium molybdate and molybdenum trioxide. For this reaction DTG shows a peak at 335 °C. However, in DTA, an endothermic peak is observed at 320 °C which is also immediately followed by an exothermic peak at 340 °C. Again, this may be attributed to the domination of oxidation of carbon monoxide into carbon dioxide. The observed weight loss is 6.31%, while the calculated value is 6.37%. The total observed weight loss for the reaction

$$Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2] \cdot 2H_2O \rightarrow SrMoO_4 + MoO_3$$

is 35.59% against the calculated value of 35.55%. The composition of the intermediate compound is well supported by the IR spectrum of the sample obtained by heating SMO isothermally at 305 °C (Fig. 1B) which, in addition to the bands characteristic of the oxalate group, shows a sharp band at 2340 cm^{-1}, attributed to the presence of carbon dioxide adsorbed onto the solid.

From the TG curve, a further weight loss is observed between 700 and 830 °C which corresponds to the complete sublimation of MoO_3, DTG showing a peak at 800 °C. DTA also shows an endothermic peak at about 800 °C which may be attributed to the sublimation accompanied by the melting of MoO_3 (m.p. = 795 °C). The observed weight loss is 30.02%, against the calculated value of 30.06%.

The end product was obtained by heating SMO isothermally at 375 as well as at 850 °C. Both these samples were characterized by chemical analysis, IR spectra and X-ray diffraction studies. The sample obtained at 375 °C is found to be a mixture of $SrMoO_4$ and MoO_3. This is evident on comparing its IR spectrum (Fig. 1C) with those of $SrMoO_4$ [9] and MoO_3 [10]. The X-ray diffraction pattern also indicates the presence of only these two phases, the *d* values matching very closely with the earlier reported data for $SrMoO_4$ [11] and MoO_3 [12]. However, both the IR spectrum (Fig. 1D) and the X-ray diffraction pattern of the sample obtained by heating SMO isothermally at 850 °C reveal the presence of only $SrMoO_4$ without any other phase. This is probably due to the complete sublimation of MoO_3.

On the basis of all these studies, we can propose the following scheme for the thermal decomposition of SMO.

$$Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$$
$$\xrightarrow{105-195\,^\circ C} Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2] + 2H_2O \quad (1)$$

$$Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2] \xrightarrow{195-220\,^\circ C} Sr[Mo_2O_5(C_2O_4)_2] + 2H_2O \quad (2)$$

$$3Sr[Mo_2O_5(C_2O_4)_2] \xrightarrow{220-300\,^\circ C} Sr_3[Mo_6O_{20}(C_2O_4)]\cdot CO_2 + 5CO + 4CO_2 \quad (3)$$

$$Sr_3[Mo_6O_{20}(C_2O_4)]\cdot CO_2 \xrightarrow{300-360\,^\circ C} 3SrMoO_4 + 3MoO_3 + CO + 2CO_2 \quad (4)$$

Equations (1) and (2) represent the dehydration of SMO while eqns. (3) and (4) represent the decomposition of anhydrous SMO to give the end product. The mechanism proposed here is a tentative one based on the results obtained from dynamic thermogravimetry and isothermal studies.

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