PREPARATION, CHARACTERIZATION AND THERMAL DECOMPOSITION OF SODIUM OXOMOLYBDENUM(VI) OXALATE

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ABSTRACT

A new Mo(VI) oxalato complex $Na_2[MoQ_3(C_2O_4)]\cdot 3\ H_2O$(SMO) is prepared and characterized by chemical analysis and IR spectral studies. Thermal decomposition studies were made using TG and DTA techniques. The dehydration takes place in two stages, two moles of water being lost in the first stage between 80 and 115°C and the third being lost in the second stage between 115 and 170°C. The anhydrous SMO is stable up to 275°C and thereafter decomposes in two stages. The first stage extends up to 335°C to give an intermediate oxalate carbonate with the tentative composition $Na_6[Mo_3O_{10}(C_2O_4)(CO_3)]$ which decomposes in the second stage between 335 and 450°C to give the end product, sodium molybdate. The end product was characterized by chemical analysis, IR and X-ray studies. The SMO is also found to be a crystalline compound.

INTRODUCTION

The preparation of different oxo complexes of molybdenum has been of great interest due to the high susceptibility of molybdenum to change its oxidation state even with minor variations in experimental conditions. Binuclear oxomolybdenum(VI) oxalates, eg., $M_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$, (M = K^+, Rb^+, Cs^+ and NH_4^+) have been prepared and studied [1]. Recently we prepared $Na_2[Mo_2O_6(C_2O_4)]\cdot 4\ H_2O$ [2], $A_2[Mo_2O_6(C_2O_4)]$ (A = K^+, NH_4^+) [3] and $Ba[MoO_3(C_2O_4)]\cdot 3\ H_2O$ [4] and a mechanism for their thermal decomposition was proposed. In addition to these, compounds such as $NaNH_4[MoO_3(C_2O_4)]\cdot 2\ H_2O$, $(Quin\ H)_2[MoO_2(C_2O_4)_2]$ [5] and $A_2[MoO_3(C_2O_4)]\cdot H_2O$ (A = K^+, NH_4^+) [6] have also been prepared and studied. The present paper deals with the preparation, characterization and thermal decomposition of a new Mo(VI) oxalato complex $Na_2[MoO_3-(C_2O_4)]\cdot 3\ H_2O$ (SMO) which could not be prepared by the usual methods employed for the preparation of most of the above mentioned compounds.

EXPERIMENTAL

All the reagents used were either of AnalaR or Proanalysi grade. To a hot solution of a mixture of 1.34 g of sodium oxalate and 1.2605 g of oxalic acid in about 200 ml of doubly-distilled water, 4.3185 g of MoO_3 (prepared by heating ammonium para-molybdate at about 400°C for 2 h) were added in small portions. The solution was filtered to remove any unreacted MoO_3. A dilute solution of sodium hydroxide was then added and the pH of the solution was adjusted to 3.0 (± 0.1). On adding excess of acetone, white precipitates were obtained which were washed with acetone and dried in vacuo.

Molybdenum in SMO was determined gravimetrically as molybdenyl oxinate and oxalate by $KMnO_4$ oxidation. Sodium was estimated on an atomic absorption spectrophotometer from Instrumentation Laboratory (model IL 751). The analysis of SMO gave: Na^+, 13.79%; Mo, 28.91%; $C_2O_4^{2-}$, 26.49% whereas the calculated values for $Na_2[MoO_3(C_2O_4)] \cdot 3\ H_2O$ are: Na^+, 13.85%; Mo, 28.90% and $C_2O_4^{2-}$, 26.51%. A good agreement between the experimental and the calculated values confirms the composition of SMO to be $Na_2[MoO_3(C_2O_4)] \cdot 3\ H_2O$.

Thermogravimetry (TG) was carried out using a Stanton-Redcroft TG 770 thermobalance at a heating rate of 3°C min^{-1}. The DTA was taken on a Stanton-Redcroft DTA-671 using ignited alumina as reference material and a heating rate of 10°C min^{-1}. Both studies were carried out in an atmosphere of static air and 5–10 mg of samples were used. 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

TABLE 1

IR and X-ray data of SMO

IR data of SMO [a]		X-Ray data of SMO [b]
Band position (cm^{-1})	Probable assignment	d values (Å) ($\lambda = 1.5405$ Å)
3500 VS, br	ν(OH) of uncoordinated water	16.427b, 3.329d
1670 VS	ν_{as}(C=O)	8.222b, 3.263c
1450 S	ν_{sym}(C–O) + ν(C–C)	6.676c, 3.050d
1300 S	ν_{sym}(C–O) + δ(O–C=O)	5.804c, 3.005c
930 S	ν_{as}(Mo=O)	5.466a, 2.873d
885 S	ν_{sym}(Mo=O)	4.101c, 2.728d
850 S	ν_{sym}(C–O) + δ(O–C=O)	3.798c, 2.708d
800 S	ν(O–Mo–O)	3.644d, 2.336d
740 VS, br	ν(O–Mo–O)	3.551d, 2.169d
485 M	Ring def. + δ(O–C=O)	3.379d, 2.041d

[a] VS = very strong; S = strong; M = medium; br = broad; sym = symmetric; as = asymmetric; δ = bending.
[b] a = strongest; b = very strong; c = strong; d = weak.

were taken on a Philips diffractometer using Cu K_α radiation. It reveals that SMO is a crystalline compound with a low symmetry class. Some of the d values are given in Table 1.

RESULTS AND DISCUSSION

The results of IR studies of SMO (Fig. 1A) are summarized in Table 1. The normal bands for coordinated oxalato groups have been assigned on the basis of existing data in the literature [7,8]. Besides these, SMO shows strong bands at 930, 885, 800 and 740 cm^{-1}, the last one being a little broad. In oxomolybdenum(VI) compounds containing both bridged and terminal oxygen atoms directly attached to molybdenum, more than one metal–oxygen stretching band has been observed [5,9–11]. Accordingly, the bands at 930 and 885 cm^{-1} have been assigned to asymmetric and symmetric Mo=O stretches, respectively. The two bands at 800 and 740 cm^{-1} are probably due to the two nonequivalent O–Mo–O groups. The compounds NaNH$_4$-[MoO$_3$(C$_2$O$_4$)]·2 H$_2$O [9], A$_2$[MoO$_3$(C$_2$O$_4$)]. H$_2$O(A = K$^+$, NH$_4^+$) [6] and Ba[MoO$_3$(C$_2$O$_4$)]·3 H$_2$O [4], have all been suggested to have an infinite chain of MoO$_6$ octahedra linked through oxygen bridges containing cis-MoO$_2$ groups. A comparison of the IR spectrum of SMO with these compounds
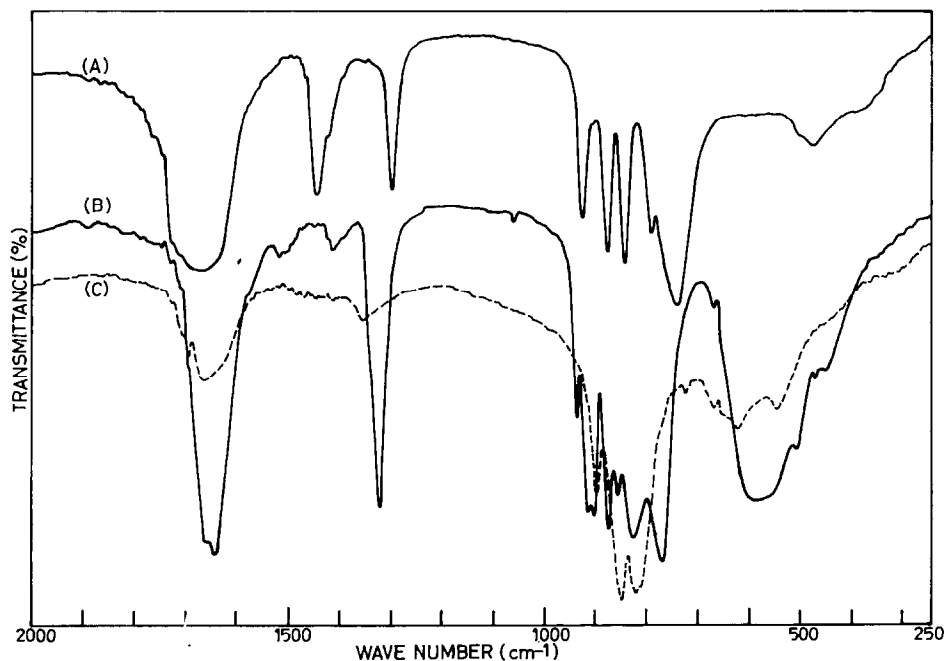

Fig. 1. IR Spectra of SMO (A), SMO heated to 340°C (B) and SMO heated to 475°C (C).
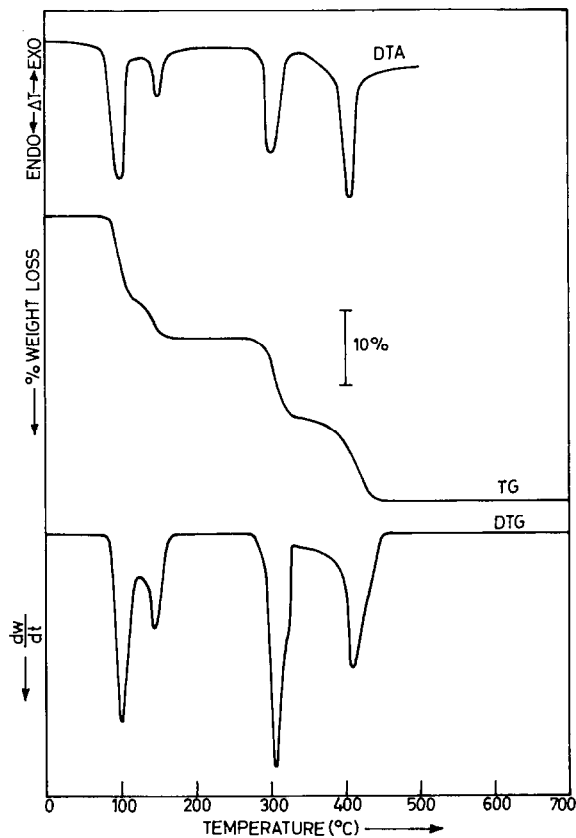
Fig. 2. DTA, TG and DTG curves of SMO in air.

suggests that SMO may also have a similar chain structure. Moreover, the $\nu(OH)$ of water occurs as a broad band around 3500 cm^{-1} indicating that the water is not coordinated to the metal.

Figure 2 gives the DTA, TG and differential thermogravimetric (DTG) curves for SMO in an atmosphere of static air. The TG curve indicates that the dehydration of SMO takes place in two steps to give the anhydrous product which decomposes in two steps to give the end product Na_2MoO_4. The various stages are discussed in detail below.

Dehydration

As seen in TG, SMO is stable up to 80°C and loses its three moles of water in two steps; the first step extending up to 115°C and the second from 115 to 170°C. This is observed in DTA as two endotherms at about 100 and 150°C, respectively. In DTG, the two stages are observed as peaks at around 100 and 145°C, respectively. The observed weight loss in the first stage is 10.71% which corresponds to the loss of two moles of water per mole of

SMO, the calculated value being 10.84%. The weight loss in the second stage corresponds to the loss of the remaining one mole of water. The observed weight loss is 5.61% compared with the calculated value of 5.42%. The difference in observed and calculated values may be attributed to the overlap of part of the two steps.
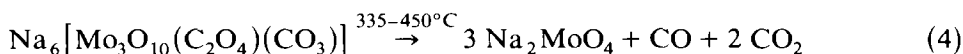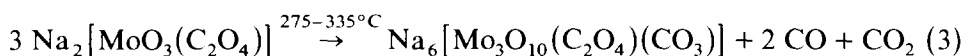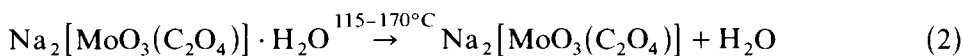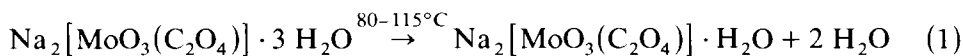
Decomposition of oxalate

The anhydrous SMO is stable up to 275°C and then decomposes in two steps. The first stage extends up to 335°C and corresponds to the loss of two moles of carbon monoxide and one mole of carbon dioxide per three moles of anhydrous SMO to give an intermediate oxalate carbonate with the tentative composition $Na_6[Mo_3O_{10}(C_2O_4)(CO_3)]$. The observed weight loss is 10.10% against the calculated value of 10.05%. DTG shows a maximum at 305°C while in DTA an endotherm at about 300°C corresponds to this reaction. This composition of the intermediate is well supported by the IR spectrum of the sample obtained by isothermal heating of SMO at 340 ± 5°C (Fig. 1B), which indicates the presence of both oxalate and carbonate. The decomposition of the intermediate product to give Na_2MoO_4 as the end product occurs in the second stage in the temperature range 335–450°C with a maximum in DTG at 410°C. This is observed in DTA as an endothermic peak at about 405°C. The observed weight loss for this stage is 11.53% whereas the calculated value is 11.64%. The total observed and calculated weight loss for the process

$$Na_2[MoO_3(C_2O_4)] \cdot 3\,H_2O \rightarrow Na_2MoO_4$$
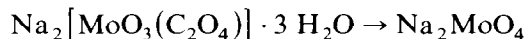
is the same, the value being 37.95%.

The end product was obtained by heating SMO isothermally at about 475°C and was characterized by chemical analysis, IR spectrum (Fig. 1C) and X-ray diffraction studies. All these studies reveal the formation of pure Na_2MoO_4 without any other phase. The IR spectrum compares well with the spectrum of sodium molybdate given in literature [12]. The observed d values also closely match with data reported earlier [13].

All these studies allow us to propose a four stage scheme for the thermal decomposition of SMO which is as follows

$$Na_2[MoO_3(C_2O_4)] \cdot 3\,H_2O \xrightarrow{80-115°C} Na_2[MoO_3(C_2O_4)] \cdot H_2O + 2\,H_2O \quad (1)$$

$$Na_2[MoO_3(C_2O_4)] \cdot H_2O \xrightarrow{115-170°C} Na_2[MoO_3(C_2O_4)] + H_2O \quad (2)$$

$$3\,Na_2[MoO_3(C_2O_4)] \xrightarrow{275-335°C} Na_6[Mo_3O_{10}(C_2O_4)(CO_3)] + 2\,CO + CO_2 \quad (3)$$

$$Na_6[Mo_3O_{10}(C_2O_4)(CO_3)] \xrightarrow{335-450°C} 3\,Na_2MoO_4 + CO + 2\,CO_2 \quad (4)$$

Equations (1) and (2) represent the two stages of dehydration to give the anhydrous SMO which then decomposes according to eqns. (3) and (4) 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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