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Note

PREPARATION OF SODIUM DIMOLYBDATE BY THE PYROLYSIS OF SODIUM OXOMOLYBDENUM(VI) OXALATE

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Thermal studies on various oxalato complexes have been of immense interest as they yield finely divided, highly reactive oxides which are usually obtained at a much lower temperature than that required in the conventional method of preparation, i.e., heating a mixture of two or more constituents [1]. A survey of the literature reveals that the compounds having the general formula $A_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$, where $A = K^+$, NH_4^+ [2] and $A = Cs^+$ [3], have been prepared and their thermal decomposition is studied, but no such information is available regarding the preparation and characterisation of $Na_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (SMO), which forms the subject of study of this paper. Sodium dimolybdate ($Na_2Mo_2O_7$), the decomposition product of SMO, is obtained at 280°C, a temperature much lower than that required in the conventional method of preparation of heating a mixture of Na_2MoO_4 and MoO_3 [4].

EXPERIMENTAL

All the reagants used were either of BDH AnalaR or Proanalysi grade. To a hot solution containing 1.2605 g of oxalic acid in about 200 ml of distilled water, 1.4395 g of MoO_3 (prepared by heating Baker Analyzed ammonium paramolybdate at about 400°C for 2h) were added in small lots. The solution was filtered to remove any unreacted MoO_3 and 0.5844 g of sodium chloride were then added. The solution was concentrated to about 30 ml and allowed to stand for about 15 days to obtain white crystals of SMO which were washed with water and dried in vacuo.

Sodium in SMO was estimated by the flame photometric method. Molybdenum was determined gravimetrically as molybdenyl oxinate and oxalate by $KMnO_4$ oxidation. Water contents were estimated on the basis of the weight loss observed during isothermal and TG studies and on the data obtained by subjecting the samples to carbon and hydrogen elemental analyses. The analysis of SMO gave: Na^+, 8.62; Mo, 36.20; $C_2O_4^{2-}$, 33.23%, whereas the calculated values for $Na_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ are: Na^+, 8.67; Mo, 36.21; $C_2O_4^{2-}$, 33.21%. These data confirm the composition of SMO to be $Na_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in an atmosphere of static air with a Stanton-Redcroft TG 770 thermobalance and a DTA 673-4 analyser, at heating rates of 2 and 5°C min^{-1}, respectively. Samples (5–10 mg) were taken in platinum crucibles for TG studies and were in quartz tubes for DTA (15–20 mg). Calcined α-alumina was used as a reference material for DTA studies. 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 diffractograms were taken on a Philips diffractometer using Cu*Kα* radiation. The magnetic measurements were taken on a Vibrating Sample Magnetometer (model VSM-155) at room temperature (21°C) using a magnetic field of 5500 Gauss.

RESULTS AND DISCUSSION

SMO is a white crystalline compound, probably of low symmetry class. The magnetic measurements indicated it to be diamagnetic, thus suggesting it to be a molybdenum(VI) compound. In addition to the bands characteristic of the coordinated oxalato group, which may be assigned on the basis of existing data in the literature [5,6], the IR spectrum of SMO (Fig. 1, spectrum A) shows three strong bands at 960, 940 and 750 cm^{-1}. The first two bands suggest the presence of metal–oxygen double bonds while the

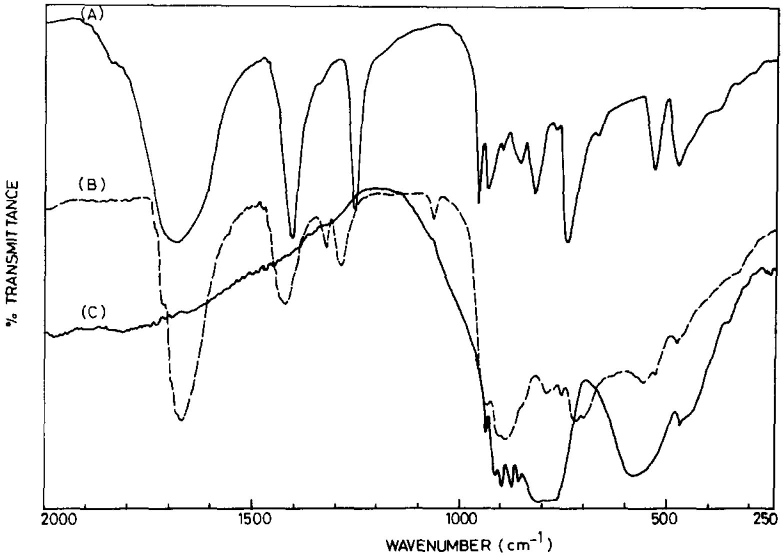

Fig. 1. IR spectra of SMO (A), SMO heated at 235°C (B), and 290°C (C).

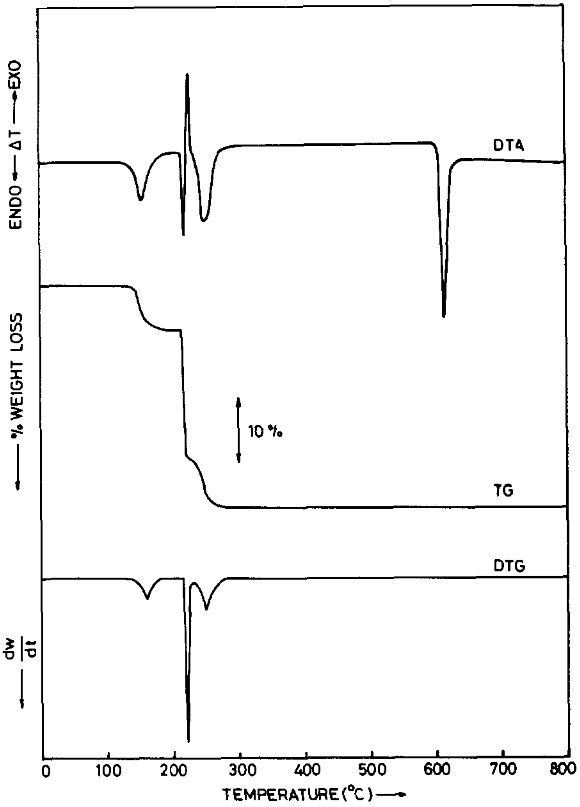

Fig. 2. DTA, TG and DTG curves of SMO.

band at 750 cm^{-1} probably results from an O–Mo–O stretch [7,8]. In addition to these, three weak bands at 900, 765 and 670 cm^{-1} have also been observed which probably appear due to the rocking, wagging and the metal–oxygen stretching vibrations, respectively, of the coordinated water [9].

Figure 2 gives the TG, DTA and DTG curves of SMO in an atmosphere of static air. The thermogram reveals that SMO loses its water in a single step which is followed by a two-stage decomposition of the anhydrous oxalate to give sodium dimolybdate ($Na_2Mo_2O_7$) as the end product. The various stages are discussed in detail below.

Dehydration

As seen on the TG curve (Fig. 2), SMO is stable up to 135°C and then loses both of its water molecules in a single step which extends up to 180°C. This is observed in DTA as an endotherm at 155°C while DTG shows a peak at 160°C. The weight loss observed on the TG curve is 6.71% against the calculated value of 6.79%. The loss of water molecules at such a high temperature could be an indication of their coordination to the metal ion. Wet chemical analysis of the sample obtained by heating SMO isothermally at 190 ± 5°C also indicated the composition of the residue to be $Na_2[Mo_2O_5(C_2O_4)_2]$.

Decomposition of oxalate

Anhydrous SMO is stable up to 215° C and then decomposes between 215 and 280°C in two stages. The first stage extends up to 230°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 oxalate–carbonate with the tentative composition $Na_6[Mo_6O_{19}(C_2O_4)(CO_3)]$. The IR spectrum of the sample obtained by heating SMO isothermally at 235 ± 5°C (Fig. 1, spectrum B) also indicates the presence of both oxalate and carbonate groups. This reaction is observed in DTG as a peak at 220°C. DTA also shows an endothermic peak at 220°C which is immediately followed by a sharp exothermic peak at 225°C. This may be attributed to the domination of oxidation of carbon monoxide liberated during decomposition. The observed weight loss is 20.00%, whereas the calculated value is 19.88%. The second stage immediately follows the first and occurs between 230 and 280°C. It involves the decomposition of $Na_6[Mo_6O_{19}(C_2O_4)(CO_3)]$ with a further loss of one mole of carbon monoxide and two moles of carbon dioxide to give the end product, both DTA and DTG showing peaks at 250°C. The weight loss observed on the TG curve is 7.29% while the calculated value is 7.30%. The total observed weight loss for the process

$$Na_2[Mo_2O_5(C_2O_4)_2(H_2O)_2] \rightarrow Na_2Mo_2O_7$$

is 34.00%, whereas the calculated value is 33.97%.

Melting

DTA shows an additional endothermic peak at 615°C which corresponds to no weight change on the TG curve. This has been attributed to the melting of the end product, the reported melting point of $Na_2Mo_2O_7$ also being 615°C [10]. Moreover, the formation of a molten product at 620 ± 5°C during isothermal studies also confirmed the peak at 615°C to be due to melting.

The end product was obtained by heating SMO isothermally at 290 ± 5°C as well as at 620 ± 5°C. Both these samples gave identical chemical analysis data, IR spectra (Fig. 1, spectrum C) and X-ray diffraction patterns. All these studies reveal the formation of pure $Na_2Mo_2O_7$ without any other phase. The bands observed in the IR spectrum closely resemble those reported for $Na_2Mo_2O_7$ [11]. The observed *d* values also closely match the earlier reported data for $Na_2Mo_2O_7$ [4].

The above results and discussions based on TG and other data allow a tentative three-stage scheme to be proposed for the thermal decomposition of SMO in air, which is as follows

$$Na_2[Mo_2O_5(C_2O_4)_2(H_2O)_2] \xrightarrow{135-180^\circ C} Na_2[Mo_2O_5(C_2O_4)_2] + 2H_2O \qquad (1)$$

$$3Na_2[Mo_2O_5(C_2O_4)_2] \xrightarrow{215-230^\circ C} Na_6[Mo_6O_{19}(C_2O_4)(CO_3)] + 5CO + 4CO_2 \qquad (2)$$

$$Na_6[Mo_6O_{19}(C_2O_4)(CO_3)] \xrightarrow{230-280^\circ C} 3Na_2Mo_2O_7 + CO + 2CO_2 \qquad (3)$$

Equation (1) represents the dehydration of SMO while eqns. (2) and (3) represent the two different stages of oxalate decomposition to give the end product.

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