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Preparation, characterization and thermal decomposition of a new oxomolybdenum(VI) oxalato complex

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Abstract

A new molybdenum(VI) complex, $K_2(NH_4)_6[Mo_8O_{24}(C_2O_4)_4]$, was prepared and characterized by chemical analysis, and IR spectral and X-ray studies. Thermal decomposition studies were made using TG, DTA and DTG techniques. The compound is anhydrous and decomposes between 538 and 633 K in two steps. The first step extends up to 603 K to give an intermediate compound with the tentative composition $K_2(NH_4)_2[Mo_8O_{24}(C_2O_4)_2]$, which decomposes in the second step to give a mixture of potassium tetramolybdate ($K_2Mo_4O_{13}$) and molybdenum trioxide (MoO_3) at 633 K. DTA also shows a peak at 800 K which corresponds to the melting of potassium tetramolybdate. An examination of the products obtained at 633 and 803 K using chemical analysis, IR spectra and X-ray studies reveals that they are identical.

INTRODUCTION

The present work is a continuation of our successful attempts to prepare, characterize and study the thermal decomposition of some new oxomolybdenum(VI) oxalato complexes [1–3]. We have synthesized yet another new oxomolybdenum(VI) oxalato complex, $K_2(NH_4)_6[Mo_8O_{24}(C_2O_4)_4]$ (PAMO), and have evolved a tentative mechanism for its thermal decomposition, the end product being a mixture of potassium tetramolybdate and molybdenum trioxide.

EXPERIMENTAL

Baker "analysed" ammonium paramolybdate and AnalaR grade potassium and ammonium oxalates were used in the preparation of PAMO. Molybdenum trioxide (5.758 g) (prepared by heating ammonium paramolybdate to about 673 K for 2 h) was added in small amounts to a hot solution containing 0.9212 g of potassium oxalate and 2.1318 g of ammonium oxalate in about 250 ml of distilled water. The solution was filtered to remove any unreacted molybdenum trioxide and was concentrated to

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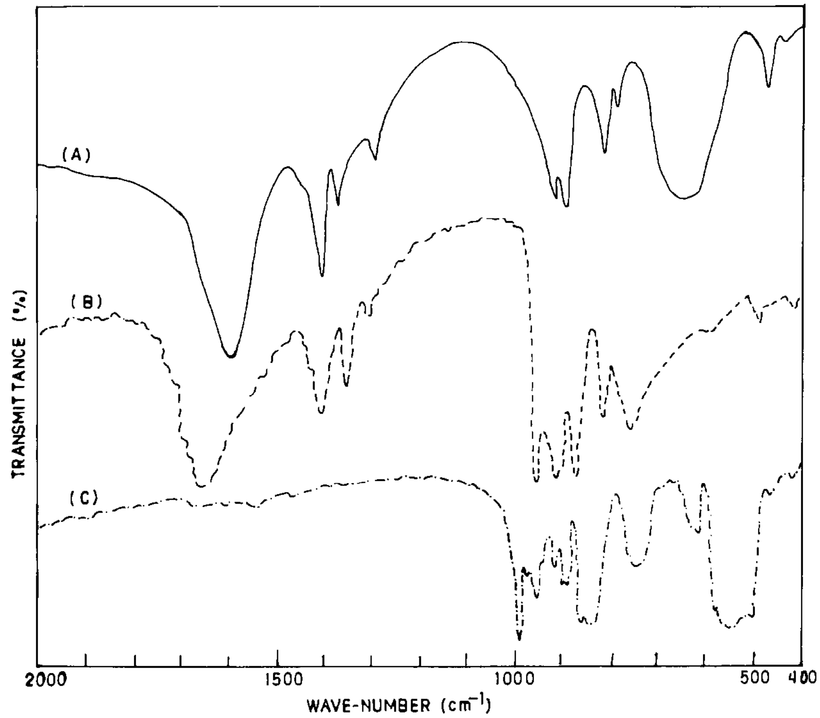

Fig. 1. IR spectra of PAMO (A), PAMO heated at 608 K (B), and 638 K (C).

about 30 ml to obtain the crystals of PAMO. The crystals were washed with distilled water and then dried in a desiccator.

The molybdenum content of the compound was determined gravimetri-

TABLE 1

IR absorption bands of PAMO and their probable assignments

Band position (cm^{-1})	Description [a]	Probable assignment [b]
3200	s, br	$\nu_{as}(NH_4^+)$
1600	vs, br	$\nu_{as}(C{=}O)$
1400	vs	$\delta(NH_4^+)$
1370	s	$\nu_{sym}(C{-}O) + \delta(O{-}C{=}O)$
1290	s	
920	s	$\nu_{as}(Mo{=}O)$
900	s	$\nu_{sym}(Mo{=}O)$
810	s	$\nu(O{-}Mo{-}O)$
790	m	$\delta(O{-}C{=}O) + \nu(M{-}O)$
660	s, br	$\nu(O{-}Mo{-}O)$
470	m	Ring deformation + $\delta(O{-}C{=}O)$
435	w	$\nu(M{-}O)$ + ring deformation

[a] vs, very strong; s, strong; m, medium; w, weak; br, broad;
[b] as, asymmetric; sym, symmetric.

cally as molybdenyl oxinate, and the oxalate was determined by $KMnO_4$ oxidation. Ammonia was determined by its liberation with aqueous alkali [4] and potassium was estimated by flame photometry. The analysis of PAMO gave 6.42% NH_4^+, 4.61% K^+, 45.40% Mo, and 20.84% $C_2O_4^{2-}$, the calculated values being 6.40%, 4.63% 45.42% and 20.83% respectively. These data confirm the composition of PAMO as $K_2(NH_4)_6[Mo_8O_{24}(C_2O_4)_4]$.

The TG, DTA and DTG were carried out using a Stanton Redcroft thermoanalyser (model STA-780 series) taking 5–10 mg of the samples in platinum crucibles. For DTA, ignited alumina was used as the reference material. The heating rate was 278 K h^{-1}. IR spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer in the range 400–4000 cm^{-1} with samples in the form of potassium bromide pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using Cu *Kα* radiation.

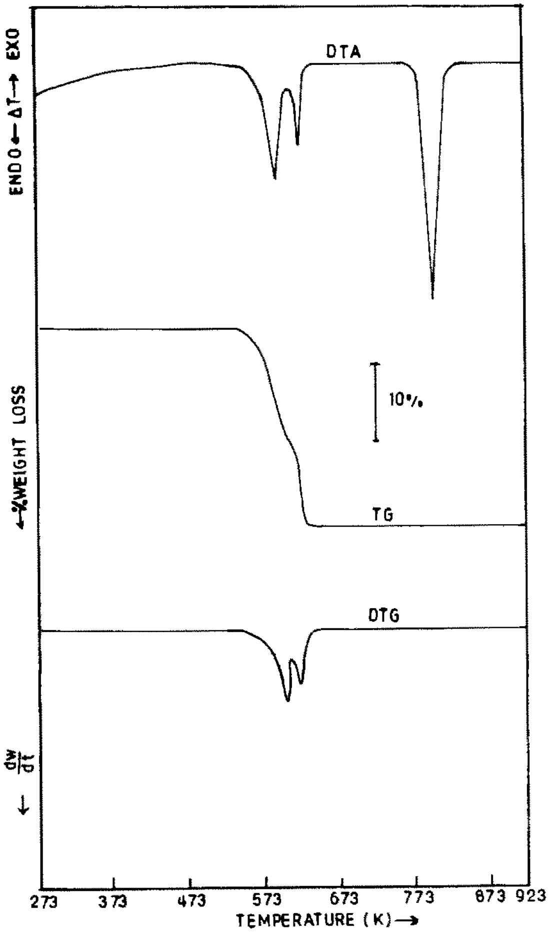

Fig. 2. DTA, TG and DTG curves of PAMO in air.

The magnetic measurements were made on a vibrating sample magnetometer, model VSM-155, at room temperature (22° C).

RESULTS AND DISCUSSION

PAMO is a white crystalline compound. The X-ray diffraction pattern shows that it probably has low symmetry. The magnetic measurements indicate that it is diamagnetic, thus suggesting that it is a molybdenum(VI) compound. The results of IR studies of PAMO (Fig. 1(A)) are summarized in Table 1. The normal bands for coordinated oxalato groups have been assigned on the basis of existing data in the literature [5,6]. In addition to these, the broad band at 3200 cm^{-1} probably results from NH_4^+ asymmetric stretching vibrations, and the band at 1400 cm^{-1} is probably due to NH_4^+ bending vibrations [7]. The two strong bands at 920 and 900 cm^{-1} suggest the presence of metal–oxygen double bonds and the bands at 810 and 660 cm^{-1} can be assigned to asymmetric and symmetric Mo–O stretching respectively [8–10].

Figure 2 shows the DTA, TG and DTG curves for PAMO in an atmosphere of static air. As seen on the TG curve, PAMO is an anhydrous compound and is stable up to 538 K. The decomposition is found to be a two-step process. The first step extends up to 603 K and corresponds to the loss of 4 mol of ammonia, 2 mol of water, 2 mol of carbon monoxide and 2 mol carbon dioxide per mole of PAMO, to give an intermediate of suggested composition $K_2(NH_4)_2[Mo_8O_{24}(C_2O_4)_2]$. This is observed in DTA and DTG as peaks at 593 K and 598 K respectively. The observed weight loss is 14.65%, the calculated value being 14.69%. The second step occurs between 603 and 633 K and corresponds to the loss of a further 2 mol of ammonia, 1 mol of water, 2 mol of carbon monoxide and 2 mol carbon dioxide to give a mixture of $K_2Mo_4O_{13}$ and MoO_3. This is seen in DTA and DTG as peaks at 623 K and 618 K respectively. The observed weight loss is 11.66%, the calculated value being 11.60%. The total weight loss observed for the process

$$K_2(NH_4)_6[Mo_8O_{24}(C_2O_4)_4] \rightarrow K_2Mo_4O_{13} + 4MoO_3 \qquad (1)$$

is 26.31%, the calculated value being 26.29%.

The tentative composition assigned to the intermediate compound formed at 603 K was confirmed by the IR spectrum of the sample obtained by heating PAMO isothermally at 608 ± 5 K (Fig. 1(B)) which, in addition to the bands characteristic of the oxalato group, also shows two bands at 3200 and 1400 cm^{-1} indicating the presence of NH_4^+.

An additional endothermic peak is observed in DTA at 800 K, which has no corresponding weight change on the TG curve. This has been attributed to the melting of potassium tetramolybdate, the reported melting point of $K_2Mo_4O_{13}$ being 803 K [11]. The product obtained on heating PAMO isothermally at 808 K solidified immediately on cooling, thus confirming that the peak at 800 K is due to the melting of potassium tetramolybdate.

PAMO samples were heated isothermally at 638 and 808 K. Both samples gave identical analysis data, IR spectra (Fig. 1(C)) and X-ray diffraction patterns. The X-ray diffraction pattern shows the peaks of both $K_2Mo_4O_{13}$ [12] and MoO_3 [13] as reported in the literature. The IR spectrum also confirms the presence of $K_2Mo_4O_{13}$ [12] and MoO_3 [14].

On the basis of all these studies, the following tentative scheme is proposed for the decomposition of PAMO in air:

$$K_2(NH_4)_6[Mo_8O_{24}(C_2O_4)_4] \xrightarrow{538-603\ K} K_2(NH_4)_2[Mo_8O_{24}(C_2O_4)_2] + 4NH_3 + 2H_2O + 2CO + 2CO_2 \tag{2}$$

$$K_2(NH_4)_2[Mo_8O_{24}(C_2O_4)_2] \xrightarrow{603-633\ K} K_2Mo_4O_{13} + 4MoO_3 + 2CO + 2CO_2 + 2NH_3 + H_2O \tag{3}$$

The mechanism proposed here is based tentatively on the results obtained from dynamic thermogravimetry and isothermal studies.

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