

PREPARATION OF POTASSIUM TRIMOLYBDATE BY THE THERMAL DECOMPOSITION OF A NEW OXOMOLYBDENUM(VI) OXALATO COMPLEX

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ABSTRACT

A new molybdenum(VI) complex $K_4(NH_4)_2[Mo_6O_{18}(C_2O_4)_3]$ (PAMO) has been prepared and characterised by chemical analysis and IR spectral studies. Thermal decomposition studies were made using TG, DTA and DTG techniques. The compound is anhydrous and stable up to 290 °C. Thereafter it decomposes in three stages. The first and the second stages occur in the temperature ranges 290–325 °C and 325–350 °C to give the intermediate compounds having the tentative compositions $K_8(NH_4)_4[Mo_{12}O_{37}(C_2O_4)_4(CO_3)]$ and $K_8[Mo_{12}O_{36}(C_2O_4)_3(CO_3)]$, respectively, the later then decomposing to give the end product $K_2Mo_3O_{10}$ at 380 °C. The end product was characterised by chemical analysis, IR spectral and X-ray studies.

INTRODUCTION

A survey of the literature reveals that although some monomolybdates [1] and dimolybdates [2,3] have been prepared by the thermal decomposition of some oxomolybdenum(VI) oxalato complexes, the preparation of trimolybdates or other higher molybdates by the pyrolysis of precursor compounds has received scant attention. The present work deals with the preparation, characterisation and thermal decomposition of a new oxomolybdenum(VI) oxalato complex, $K_4(NH_4)_2[Mo_6O_{18}(C_2O_4)_3]$ (PAMO), which gives potassium trimolybdate, $K_2Mo_3O_{10}$, as the end product.

EXPERIMENTAL

Baker analysed ammonium para-molybdate and AnalaR grade potassium and ammonium oxalates were used in the preparation of PAMO. To a hot solution containing 2.6846 g of potassium oxalate and 1.4212 g of ammonium oxalate in about 250 ml of distilled water, 8.6370 g of molybdenum trioxide (prepared by heating ammonium para-molybdate to about 400 °C

for 2 h) were added in small aliquots. The solution was filtered to remove any unreacted molybdenum trioxide and the clear solution was concentrated to about 30 ml to obtain the crystals of PAMO. The crystals were washed with distilled water and then air dried in a desiccator.

Molybdenum in the compound was determined gravimetrically as molybdenyl oxinate and oxalate by KMnO_4 oxidation. Ammonia was determined by its liberation with aqueous alkali [4] and potassium was estimated by the flame photometric method. The analysis of PAMO gave: NH_4^+ , 2.71%; K^+ , 11.81%; Mo, 43.62%; $\text{C}_2\text{O}_4^{2-}$, 20.00%, whereas the calculated values for PAMO are NH_4^+ , 2.73%; K^+ , 11.84%; Mo, 43.60%; $\text{C}_2\text{O}_4^{2-}$, 20.01%. These data confirm the composition of PAMO to be $\text{K}_4(\text{NH}_4)_2[\text{Mo}_6\text{O}_{18}(\text{C}_2\text{O}_4)_3]$.

Thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) were carried out on Stanton Redcroft STA-780 series model taking 5–10 mg of the samples in platinum crucibles. For DTA, ignited alumina was used as the reference material. The heating rate was $10^\circ\text{C min}^{-1}$. IR spectra were recorded on a Beckman IR-20 double beam instrument in the range $250\text{--}4000\text{ cm}^{-1}$ with samples in the form of potassium bromide pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using $\text{Cu K}\alpha$ radiation.

RESULTS AND DISCUSSION

PAMO is a white powder and its X-ray diffraction pattern reveals that it is a crystalline compound. The results of IR studies of PAMO (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 [5,6]. Besides 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 930 and 900 cm^{-1} suggest the presence of metal–oxygen double bonds and the bands at 820 and 650 cm^{-1} can be assigned to the asymmetric and symmetric Mo–O stretches respectively [8–10].

Figure 2 gives 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 290°C . The decomposition is found to be a three-step process. The first step extends up to 325°C and corresponds to the loss of two moles of carbon monoxide and one mole of carbon dioxide per two moles of PAMO to give an intermediate with the tentative composition $\text{K}_8(\text{NH}_4)_4[\text{Mo}_{12}\text{O}_{37}(\text{C}_2\text{O}_4)_4(\text{CO}_3)]$. This was observed both in DTA and DTG as peaks at 320°C . The observed weight loss was 3.79% as compared to the calculated value of 3.78%. The second step occurs between $325\text{--}350^\circ\text{C}$ and corresponds to a further loss of one mole of carbon

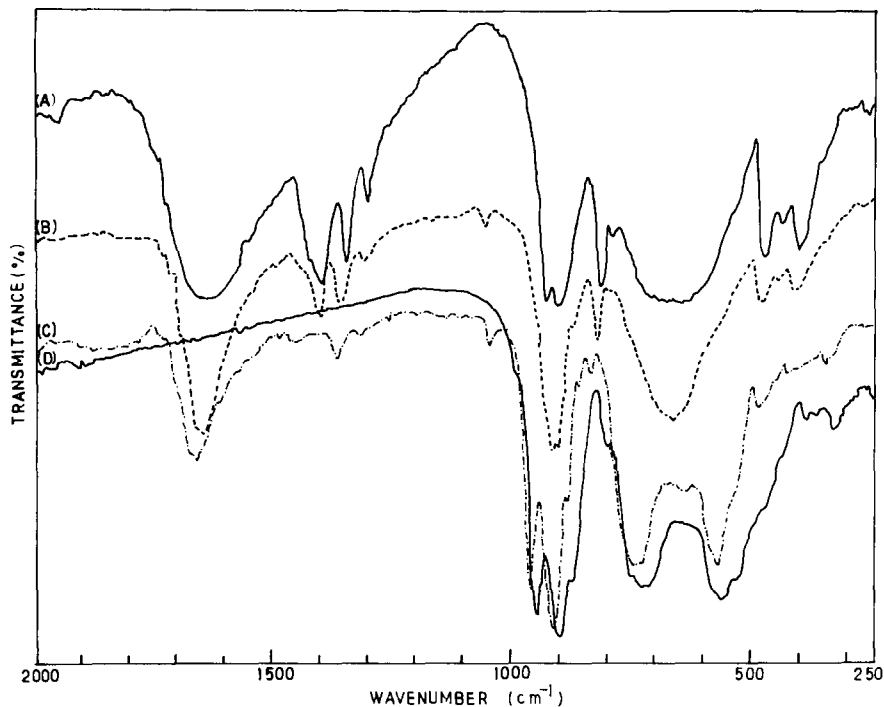


Fig. 1. IR spectra of PAMO at room temperature (A), at 325° C (B), at 355° C (C), and at 385° C (D).

TABLE 1

IR absorption bands of PAMO and their probable assignments

Band position		Probable assignment
Frequency (cm ⁻¹)	Strength ^a	
3200	s, br	ν as (NH ₄ ⁺)
1660	vs, br	ν as (C=O)
1400	vs	δ (NH ₄ ⁺)
1350	s	ν sym(C-O) + δ (O-C=O)
1300	s	
930	s	ν as Mo=O
900	s	ν sym Mo=O
820	s	ν (O-Mo-O)
790	m	δ (O-C=O) + ν (M-O)
650	s, br	ν (O-Mo-O)
470	m	Ring def. + δ (O-C=O)
435	w	ν (M-O) + ring def.
400	m	δ (O-C=O)

^a vs = very strong, s = strong, m = medium, w = weak, br = broad, as = asymmetric, sym = symmetric.

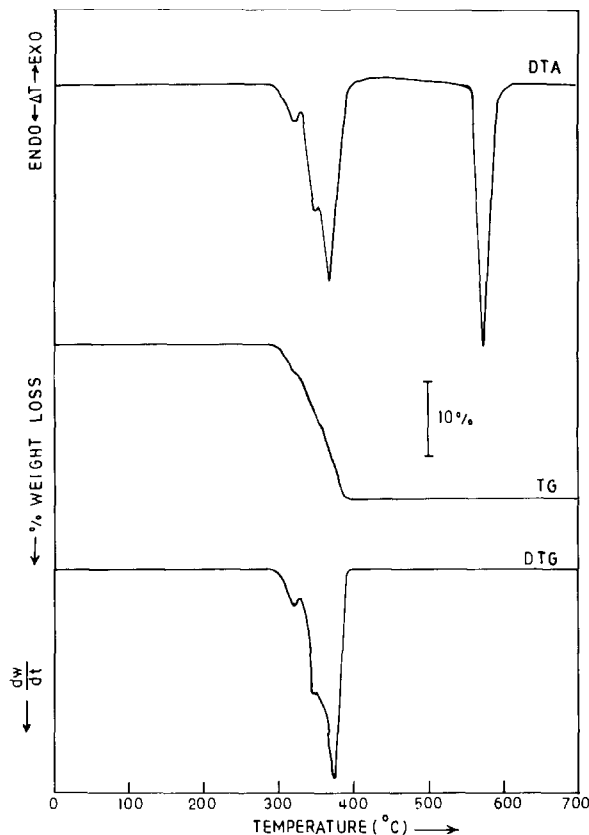
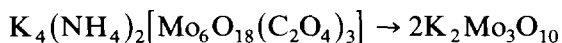


Fig. 2. DTA-TG and DTG curves of PAMO in air.

monoxide and dioxide each, two moles of water and four moles of ammonia to give another intermediate with the tentative composition $K_8[Mo_{12}O_{36}-(C_2O_4)_3(CO_3)]$. The peaks at $350^\circ C$ in DTA and $345^\circ C$ in DTG correspond to this step. The observed weight loss was 6.60% against the calculated value of 6.67%. $K_8[Mo_{12}O_{36}-(C_2O_4)_3(CO_3)]$ decomposes in the third step that extends up to $380^\circ C$ and loses three moles of carbon monoxide and four moles of carbon dioxide to give the end product $K_2Mo_3O_{10}$. This is seen in DTA and DTG as peaks at 365 and $370^\circ C$ respectively. The observed weight loss was 9.90% as compared with the calculated value of 9.84%. The difference between the observed and the calculated values in the second and the third step may be attributed to the overlap of part of the two steps. The total observed weight loss for the process



was 20.29%, the calculated value being the same.

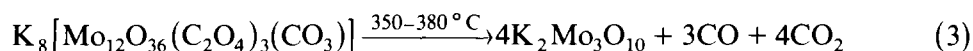
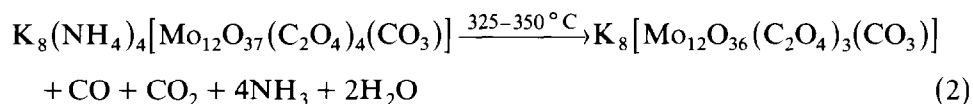
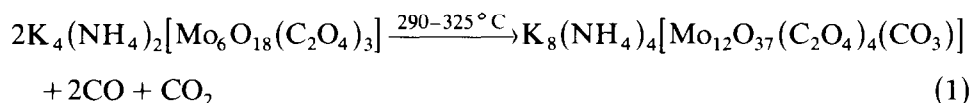
The tentative compositions assigned to the intermediate compounds formed at 325 and $350^\circ C$ are well supported by the IR spectra of the

samples obtained by heating PAMO isothermally at 325 ± 5 (Fig. 1B) and $355 \pm 5^\circ\text{C}$ (Fig. 1C) respectively, both experiments giving bands characteristic of oxalate and carbonate groups, but the former also showing additional strong bands at 3200 and 1400 cm^{-1} which are characteristic of NH_4^+ [7].

An additional endothermic peak is observed in DTA at 570°C which does not correspond to any weight change on the TG curve. Thus the peak which is evidently due to some physical change, has been attributed to the melting of the end product, the reported melting point of $\text{K}_2\text{Mo}_3\text{O}_{10}$ also being the same [11]. This was further confirmed by heating PAMO isothermally at $575 \pm 5^\circ\text{C}$ whereupon a molten product was obtained which solidified immediately to give a white crystalline compound.

The end product was obtained by heating PAMO isothermally at 385 and 575°C , the latter giving a molten product which solidified to a white crystalline compound. Both of them gave identical chemical analysis data, IR spectra (Fig. 1D) and X-ray diffraction patterns. The IR spectrum is identical to that reported in the literature [12]. The observed d values also match very closely with the earlier reported data for $\text{K}_2\text{Mo}_3\text{O}_{10}$ [13].

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



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