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

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ABSTRACT

A new molybdenum(VI) complex $K_2(NH_4)_2[Mo_4O_{12}(C_2O_4)_2]$ was prepared and characterized by chemical analysis, IR spectral and X-ray studies. Thermal decomposition studies were made using TG, DTA and DTG techniques. The compound is anhydrous and decomposes between 583 and 643 K in two stages. The first stage extends up to 613 K to give an intermediate compound with the tentative composition $K_6(NH_4)_2[Mo_{12}O_{36}(C_2O_4)_4]$, which decomposes in the second stage to give the end product, potassium tetramolybdate. The end product was characterized by chemical analysis, IR spectral and X-ray studies.

INTRODUCTION

A survey of the literature reveals that although some lower molybdates [1,2] have been prepared by the thermal decomposition of some oxomolybdenum(VI) oxalato complexes, the preparation of higher molybdates by the pyrolysis of precursor compounds has received scant attention. The present work deals with the preparation, characterization and thermal decomposition of a new oxomolybdenum(VI) oxalato complex, $K_2(NH_4)_2[Mo_4O_{12}(C_2O_4)_2]$ (PAMO), which gives potassium tetramolybdate ($K_2Mo_4O_{13}$) as the end product.

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 1.8424 g of potassium oxalate and 1.4212 g of ammonium oxalate in about 250 ml of distilled water. 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 double distilled water and then air dried in a desiccator.

Molybdenum in the compound was determined gravimetrically as molybdenyl oxinate, and oxalate was determined by $KMnO_4$ oxidation. Ammonia was determined by its liberation with aqueous alkali [3] and potassium was estimated by flame photometry. The analysis of PAMO gave: NH_4^+, 4.18%; K^+, 9.01%; Mo, 44.28% and $C_2O_4^{2-}$, 20.30%, the calculated values being 4.16, 9.03, 44.31 and 20.32% respectively. These data confirm that the composition of PAMO is $K_2(NH_4)_2[Mo_4O_{12}(C_2O_4)_2]$.

TG, DTA and DTG were carried out on a Stanton Redcroft STA-780 series model with 5–10 mg of the samples in platinum crucibles. For DTA, ignited alumina was used as the reference material. The heating rate was 283 $K min^{-1}$. 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 potassium bromide pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

As indicated by the X-ray diffraction pattern, PAMO, which is white, is a crystalline compound probably with a lower symmetry. 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 literature data [4,5]. 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 [6]. 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 asymmetric and symmetric Mo–O stretching, respectively [7–9].

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 583 K. The decomposition is found to be a two-step process. The first step extends up to 613 K and corresponds to the loss of 4 moles of ammonia, 2 moles of water, and 2 moles each of carbon monoxide and dioxide per 3 moles of PAMO, to give an intermediate with the tentative composition $K_6(NH_4)_2[Mo_{12}O_{36}(C_2O_4)_4]$. This is observed in both DTA and DTG as peaks at 598 K. The observed weight loss is 9.52%, compared with the calculated value of 9.55%. The second step occurs between 613 and 643 K and corresponds with the loss of a further 2 moles of ammonia, 1 mole of water and 4 moles each of carbon monoxide and
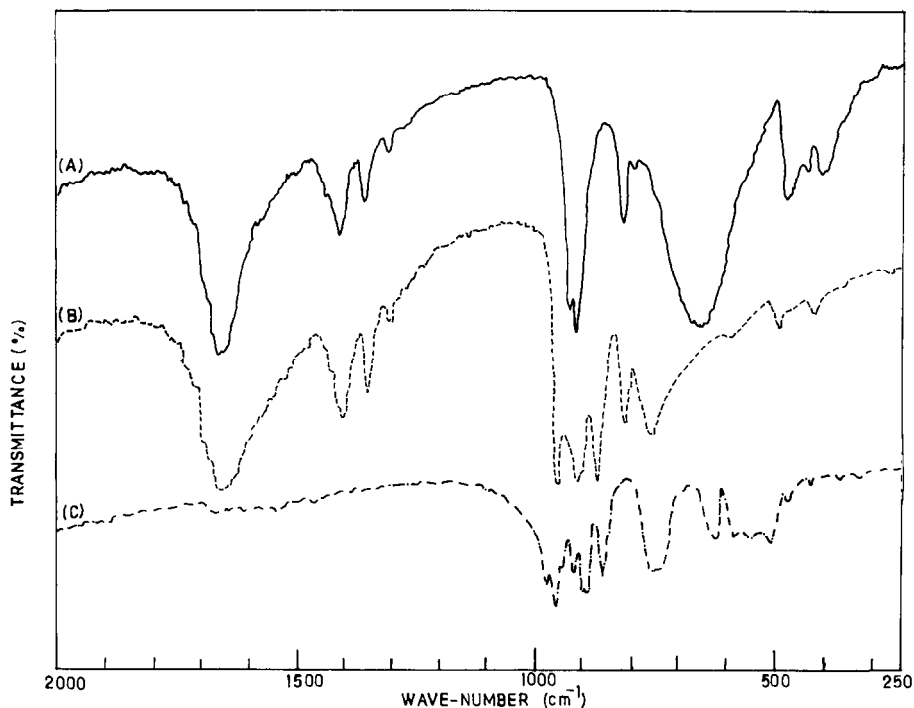
Fig. 1. (A) IR spectra of PAMO; (B) PAMO heated at 613 K and (C) PAMO heated at 648 K.

TABLE 1

IR absorption bands of PAMO and their probable assignments

Band position (cm^{-1})	Description	Probable assignment
3200	s, br	ν as (NH_4^+)
1600	vs, br	ν as $(C=O)$
1410	vs	$\delta(NH_4^+)$
1360	s ⎱	ν sym$(C–O) + \delta(O–C=O)$
1310	s ⎰	
925	s	ν as Mo=O
910	s	ν sym Mo=O
820	s	$\nu(O–Mo–O)$
790	m	$\delta(O–C=O) + \nu(M–O)$
650	s, br	$\nu(O–Mo–O)$
470	m	ring def. $+ \delta(O–C=O)$
435	w	$\nu(M–O) +$ ring def.
400	m	$\delta(O–C=O)$

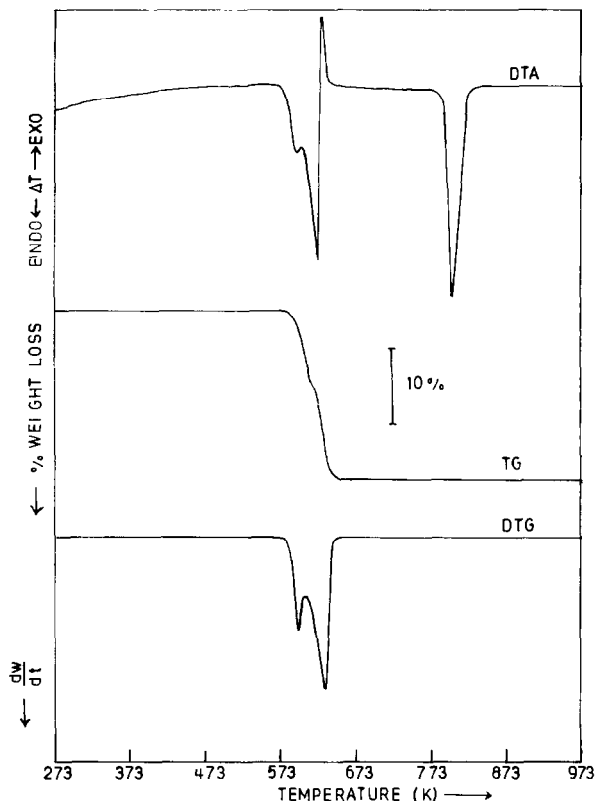vs = very strong, s = strong, m = medium, w = weak, br = broad, as = asymmetric, sym = symmetric.

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

dioxide, to give the end product $K_2Mo_4O_{13}$. This is seen in DTG as the peak at 633 K. However, in DTA an endothermic peak at 623 K is immediately followed by a sharp exothermic peak at 628 K, which probably results from the dominant oxidation of carbon monoxide liberated during the primary decomposition process. The observed weight loss is 13.10%, compared with the calculated value of 13.09%. The total weight loss observed for the process

$$K_2(NH_4)_2[Mo_4O_{12}(C_2O_4)_2] \rightarrow K_2Mo_4O_{13}$$
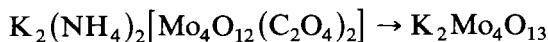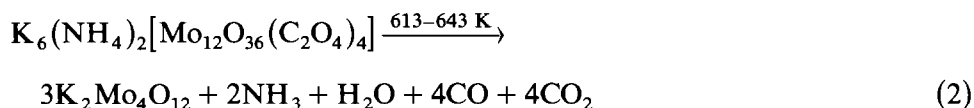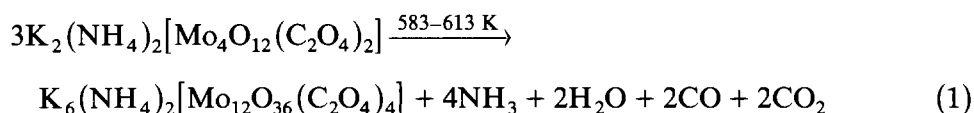
is 22.62%, compared with the calculated value of 22.64%.

The tentative composition assigned to the intermediate compound formed at 613 K is confirmed by the IR spectra of the sample obtained by heating PAMO isothermally at 613 ± 5 K (Fig. 1(B)), which, in addition to the bands characteristic of the oxalato group, shows two strong bands at 3200 and 1400 cm^{-1} indicating the presence of NH_4^+.

An additional endothermic peak is observed in DTA at 803 K, which corresponds with no change on the TG curve. This has been attributed to the melting of the end product, the reported melting point of $K_2Mo_4O_{13}$

being the same [10]. This was further confirmed by heating PAMO isothermally at 808 ± 5 K when a molten product was obtained that immediately solidified to a white crystalline compound.

The end product was obtained by heating PAMO isothermally at 648 and 808 K, the latter giving a molten product that solidified to a white crystalline compound. Both these samples give identical chemical analysis data, IR spectra (Fig. 1(C)) and X-ray diffraction patterns. The IR spectrum is identical to that reported in the literature [11]. The observed d values also match very closely with the earlier reported data for $K_2Mo_4O_{13}$ [11].

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

$$3K_2(NH_4)_2[Mo_4O_{12}(C_2O_4)_2] \xrightarrow{583-613 \text{ K}}$$

$$K_6(NH_4)_2[Mo_{12}O_{36}(C_2O_4)_4] + 4NH_3 + 2H_2O + 2CO + 2CO_2 \qquad (1)$$

$$K_6(NH_4)_2[Mo_{12}O_{36}(C_2O_4)_4] \xrightarrow{613-643 \text{ K}}$$

$$3K_2Mo_4O_{12} + 2NH_3 + H_2O + 4CO + 4CO_2 \qquad (2)$$

Equation (1) represents the first stage of decomposition of oxalate to give the intermediate compound, which then decomposes according to eqn. (2) to give the end product.

It should be realized, of course, that structural interpretations based on weight loss phenomena in TG are inherently limited in scope and thus the intermediate proposed need not represent an exact stable composition. The composition of residues isolated in isothermal experiments may often not match the apparent composition assigned on the basis of weight loss measurements.

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