

IR AND THERMAL STUDIES ON A NEW OXOMOLYBDENUM(VI) OXALATO COMPLEX

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A new molybdenum(VI) oxalato complex $K_4(NH_4)_{10}[Mo_{14}O_{42}(C_2O_4)_7]$ (PAMO) was prepared and characterized by chemical analysis, IR spectral and X-ray studies. Its thermal decomposition was studied using TG, DTA and DTG techniques. The compound is anhydrous and decomposes between 235° and 335°C in three steps. The first and the second steps occur in the temperature ranges 235°–290°C and 290–310°C to give the intermediate compounds having the tentative compositions $K_4(NH_4)_8[Mo_{14}O_{42}(C_2O_4)_6]$ and $K_2(NH_4)_2[Mo_{14}O_{42}(C_2O_4)_3]$, respectively, the later than decomposing to give a mixture of potassium tetramolybdate and molybdenum trioxide at 335°C. DTA also shows a peak at 530°C which corresponds to the melting of potassium tetramolybdate. An examination of the products obtained at 340° and 535°C by chemical analysis, IR spectra and X-ray studies reveals them to be identical.

Keywords: complex, IR spectra, thermal analysis, X-ray

Introduction

The present work is in continuation with our successful attempts to prepare, characterize and study the thermal decomposition of some new oxomolybdenum(VI) oxalato complexes [1–3]. This time we have synthesized yet another new oxomolybdenum(VI) oxalato complex $K_4(NH_4)_{10}[Mo_{14}O_{42}(C_2O_4)_7]$ (PAMO) and evolved a tentative mechanism of its thermal decomposition, the end product being a mixture of potassium tetramolybdate and molybdenum trioxide.

Experimental details

Baker analysed ammonium para-molybdate and AnalaR grade potassium and ammonium oxalates were used in the preparation of PAMO. To a hot solution containing 1.4738 g of potassium oxalate and 2.8424 g of ammonium oxalate in about 250 ml of distilled water, 8.0612 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 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 and potassium was estimated by flame photometry. The analysis of PAMO gave: NH_4^+ , 6.06%; K^+ , 5.28%; Mo, 45.27% and $\text{C}_2\text{O}_4^{2-}$, 20.78%, the calculated values being 6.08%, 5.27%, 45.26% and 20.76% respectively.

These data show that there is no noticeable deviation in the composition of PAMO from $\text{K}_4(\text{NH}_4)_{10}[\text{Mo}_{14}\text{O}_{42}(\text{C}_2\text{O}_4)_7]$.

Table 1 IR absorption bands of PAMO and their probable assignments

Frequency / cm^{-1}	Band type*	Probable assignment
3200	s, br	v as (NH_4^+)
1660	vs, br	v as (C=O)
1400	vs	δ (NH_4^+)
1360	s	v sym (C–O)+ δ (O–C=O)
1310	s	
920	s	v as (Mo=O)
900	s	v sym (Mo=O)
840	s	v (O–Mo–O)
810	m	δ (O–C=O) +v (M–O)
660	s, br	v (O–Mo–O)
480	m	ring def. + δ (O–C=O)
430	w	v (M–O) +ring def.

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

TG, DTA and DTG were carried out using a Stanton Redcroft thermoanalyser (model STA-780 series) taking 5–10 mg samples in platinum crucibles. For DTA, alumina was used as the reference material. The heating rate was 10 deg min^{-1} . IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer in the

range $400\text{--}4000\text{ cm}^{-1}$ with samples in the form of potassium bromide pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using $\text{CuK}\alpha$ radiation. The magnetic measurements were taken on a vibrating sample magnetometer (model VSM-155) at room temperature (23°C), using a magnetic field of 5500 Gauss.

Results and discussion

PAMO is a white crystalline compound and the X-ray diffraction pattern shows that probably it has a lower symmetry. The magnetic measurements indicate it to be a diamagnetic suggesting that it is a molybdenum(VI) compound. The result of IR studies of PAMO are summarized in Table 1. The normal bands for coordinated oxalato groups have been assigned on the basis of existing data in the literature [4, 5]. In addition, the broad band at 3200 cm^{-1} probably results from

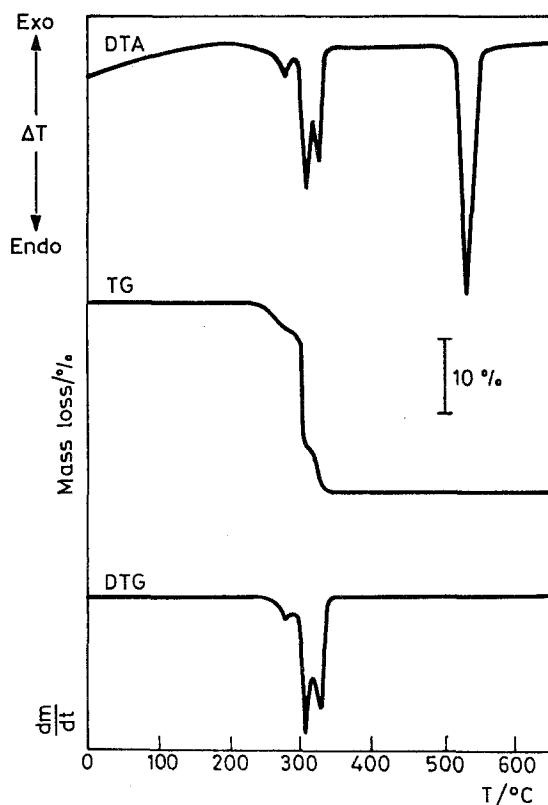


Fig. 1 DTA, TG and DTG curves of PAMO in air

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 920 and 900 cm^{-1} suggest the presence of metal-oxygen double bonds and the bands at 840 and 660 cm^{-1} can be assigned to the asymmetric and symmetric M-O stretches respectively [7-9].

Figure 1 shows the DTA, TG and DTG curves for PAMO in an atmosphere of static air. As seen on the TG curve, the PAMO is an anhydrous compound and is stable up to 235°C . The decomposition is found to be a three step process. The first step extends up to 290°C and corresponds to the loss of two moles of ammonia, one mole of water, one mole of carbon monoxide and one mole of carbon dioxide per mole of PAMO to give an intermediate with the tentative composition $\text{K}_4(\text{NH}_4)_8[\text{Mo}_{14}\text{O}_{42}(\text{C}_2\text{O}_4)_6]$. This is observed in DTA and DTG as small peaks at 275°C . The observed wt loss is 4.20% compared with the calculated value of 4.18%. The second step occurs between 290° and 310°C and corresponds to a further loss of six moles of ammonia, three moles of water, three moles of carbon monoxide and three moles of carbon dioxide to give another intermediate with the tentative composition $\text{K}_4(\text{NH}_4)_2[\text{Mo}_{14}\text{O}_{42}(\text{C}_2\text{O}_4)_3]$. This is observed both in DTA and DTG, as peaks at 305°C . The observed weight loss is 12.60% compared with the calculated value of 12.54%. $\text{K}_4(\text{NH}_4)_2[\text{Mo}_{14}\text{O}_{42}(\text{C}_2\text{O}_4)_3]$ decomposes in third step that extends up to 335°C and loses two moles of ammonia, one mole of water, three moles of carbon monoxide and dioxide each to give a mixture of $\text{K}_2\text{Mo}_4\text{O}_{13}$ (potassium tetramolybdate) and MoO_3 (molybdenum trioxide) as the end product. The peaks at 325°C in DTA and 330°C in DTG correspond to this reaction. The

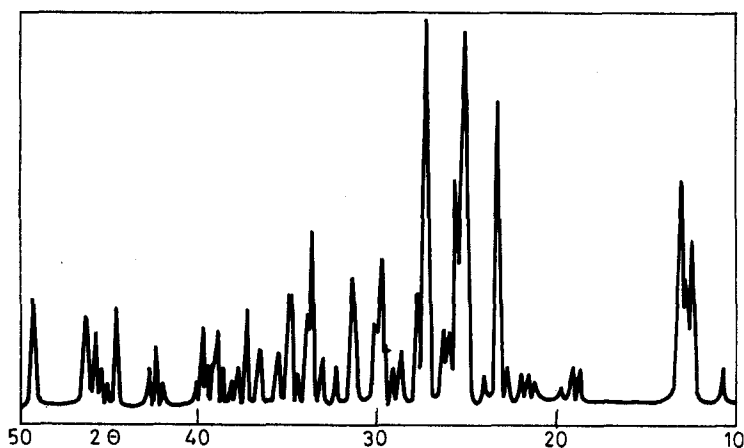
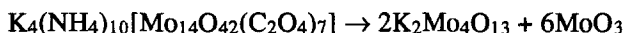


Fig. 2 X-ray power diffraction pattern of the decomposition product of PAMO

observed weight loss is 9.00% as compared to the calculated value of 9.03%. The total weight loss observed for the process:

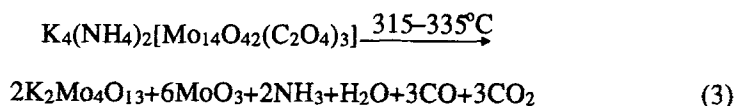
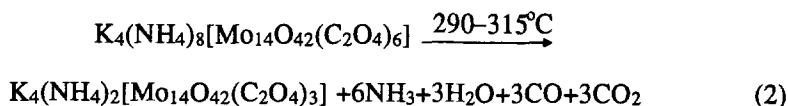
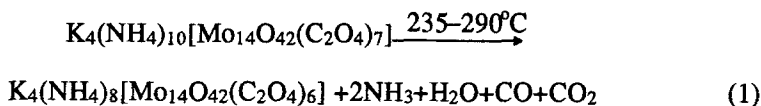


is 25.8% compared with a calculated value of 25.75%.

The tentative composition assigned to the intermediate compounds formed at 290° and 310°C are well supported by the IR spectra of the samples obtained by heating PAMO isothermally at these temperatures. Both of them indicate the presence of oxalate as well as NH_4^+ group [6].

DTA shows an additional endothermic peak at 530°C (Fig. 1) with no corresponding weight change observed on the TG curve. This has been attributed to the melting of potassium tetramolybdate ($\text{K}_2\text{Mo}_4\text{O}_{13}$). The reported melting point was also the same [10]. The product obtained on heating PAMO isothermally at 535°±5°C solidified immediately on cooling, thus confirming the peak at 530°C to be due to the melting of potassium tetramolybdate.

PAMO samples were heated isothermally at 340° and 535°C. Both these samples gave identical chemical analysis data, IR spectra and X-ray diffraction patterns (Fig. 2). The X-ray diffraction pattern shows the lines of both $\text{K}_2\text{Mo}_4\text{O}_{13}$ [11] and MoO_3 [12] as reported in the literature. The IR spectrum also confirms the presence of $\text{K}_2\text{Mo}_4\text{O}_{13}$ [11] and MoO_3 [13]. On the basis of all these studies, the following scheme is proposed for the decomposition of PAMO in air:



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

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Zusammenfassung — Ein neuer Molybdän(VI)oxalatokomplex $K_4(NH_4)_{10}[Mo_{14}O_{42}(C_2O_4)]$ wurde hergestellt und durch chemische Analyse, IR-spektroskopischen und Röntgendiffraktionsuntersuchungen beschrieben. Seine thermische Zersetzung wurde mittels TG, DTA und DTG-Techniken untersucht. Die Verbindung ist wasserfrei und zersetzt sich zwischen 235° und 335°C. Der erste und zweite Schritt verläuft in den Temperaturbereichen 235°–290°C und 290°–310°C und liefert die Zwischenprodukte mit der vorläufigen Zusammensetzung $K_4(NH_4)_8[Mo_{14}O_{42}(C_2O_4)_6]$ und $K_4(NH_4)_2[Mo_{14}O_{42}(C_2O_4)_3]$, die sich dann später bei 335°C zu einem Gemisch aus Kaliumtetramolybdat und Molybdäntrioxid zersetzen. Auch DTA zeigt einen Peak bei 530°C, der für das Schmelzen von Kaliumtetramolybdat steht. Eine Untersuchung der bei 340° bzw. bei 535°C erzielten Produkte durch chemische, IR-spektroskopische und röntgenografische Verfahren erwies beide als identisch.