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PREPARATION AND THERMAL DECOMPOSITION OF SOME OXOMOLYBDENUM(VI) OXALATES

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ABSTRACT

Anionic oxomolybdenum(VI) oxalates having the general formula $A_2[Mo_2O_6(C_2O_4)]$, where $A = K^+$ and NH_4^+, are prepared and characterized by chemical analysis and IR spectra, and their thermal decomposition studied using TG and DTA techniques. Both the compounds are anhydrous and the decomposition of oxalate takes place in a single step. The ammonium compound decomposes between 255 and 320°C to give MoO_3 as the end product, while the potassium compound decomposes between 300 and 380°C to give $K_2Mo_2O_7$ as the end product. Both the products were characterized by chemical analysis, IR and X-ray studies. The X-ray diffraction patterns of the two oxalato complexes confirm that they are crystalline compounds.

INTRODUCTION

Molybdenum(VI) forms a variety of anionic oxomolybdenum oxalates of which the following compounds have been prepared and characterized [1]: $NaNH_4[MoO_3(C_2O_4)]\cdot 2\,H_2O$, $K_2[Mo_2O_5(C_2O_4)_2]\cdot 2\,H_2O$ and (Quin H)$_2$-$[MoO_2(C_2O_4)_2]$. $A_2[MoO_3(C_2O_4)]$ (where $A = K^+$ and NH_4^+) have also been prepared and studied [2]. The present work deals with the preparation, characterization and thermal decomposition of two new molybdenum(VI) oxalate complexes having the general formula $A_2[Mo_2O_6(C_2O_4)]$, where $A = K^+$ and NH_4^+. Both these complexes have a molybdenum : oxalate ratio of 2 : 1 which has not been observed in any of the above-mentioned compounds. The ammonium compound (AMO) gives MoO_3 as the end product, while $K_2Mo_2O_7$ has been found to be the end product in the case of the potassium compound (PMO). The preparation of MoO_3 can be used as a tool for the purification of MoO_3. Impure MoO_3 is dissolved in ammonium oxalate to give AMO which when heated to about 325°C gives pure MoO_3. Potassium dimolybdate, $K_2Mo_2O_7$, can be prepared in a pure state by the thermal decomposition of PMO which takes place at a much lower temperature than that which is needed in the usual method of heating a mixture of potassium carbonate and molybdenum trioxide in the required proportions.

EXPERIMENTAL

Baker analyzed ammonium *para*-molybdate and AnalaR grade potassium oxalate and ammonium oxalate were used in the preparation of AMO and PMO as follows. To a hot solution of potassium oxalate (1.842 g)/ammonium oxalate (1.421 g) in about 400 ml of distilled water, 2.879 g of MoO_3 (prepared by heating ammonium *para*-molybdate to about 400°C for 2 h) were added in small lots. The solution was filtered to remove any unreacted MoO_3 and the clear solution was concentrated. The crystals of the complex oxalate started to separate during concentration, and were washed with water and air dried in a desiccator.

TABLE 1

X-ray data of AMO and PMO

d Values (Å^0), $\lambda = 1.5405$ Å	
AMO	PMO
6.177 [a]	6.000 [b]
4.870 [c]	4.791 [b]
3.846 [b]	3.810 [c]
3.652 [c]	3.689 [d]
3.424 [b]	3.450 [b]
3.148 [c]	3.395 [c]
3.005 [b]	3.376 [c]
2.686 [c]	3.145 [c]
2.640 [b]	2.997 [a]
2.287 [c]	2.682 [c]
2.273 [c]	2.577 [c]
2.165 [c]	2.383 [c]
2.140 [c]	2.273 [c]
1.929 [b]	2.199 [d]
1.899 [c]	2.138 [b]
1.817 [c]	2.088 [c]
1.736 [c]	1.967 [d]
1.717 [c]	1.899 [c]
1.675 [c]	1.813 [b]
1.626 [c]	1.736 [c]
1.594 [c]	1.654 [c]
1.570 [c]	1.554 [c]
1.517 [c]	1.510 [c]
1.430 [c]	1.381 [d]
1.336 [c]	1.345 [d]

[a] Strongest.

[b] Very strong.

[c] Strong.

[d] Weak.

Molybdenum in the compounds was determined gravimetrically as molybdenyl oxinate, and oxalate by $KMnO_4$ oxidation. Ammonia in AMO was determined by its liberation with aqueous alkali [3] and potassium in PMO was estimated by flame photometric method. The analysis of AMO gave: NH_4^+, 8.68%; Mo, 46.51% and $C_2O_4^{2-}$, 21.32%, whereas the calculated values for $(NH_4)_2[Mo_2O_6(C_2O_4)]$ are: NH_4^+, 8.73%; Mo, 46.58% and $C_2O_4^{2-}$, 21.36%. The results of the chemical analysis for PMO are: K^+, 17.08%; Mo, 42.20% and $C_2O_4^{2-}$, 19.37%, whereas the calculated values for $K_2[Mo_2O_6(C_2O_4)]$ are: K^+, 17.22%; Mo, 42.25% and $C_2O_4^{2-}$, 19.37%. These data show that there are no noticeable deviations from the compositions $(NH_4)_2[Mo_2O_6(C_2O_4)]$ and $K_2[Mo_2O_6(C_2O_4)]$, for AMO and PMO, respectively.

Thermogravimetry (TG) was carried out using a Stanton-Redcroft TG 770 thermobalance, taking 5–10 mg samples in platinum crucibles. Differential thermal analysis was carried out on a Stanton-Redcroft DTA 673-4 using about 2.0 cm long quartz tubes as sample containers and taking about 20 mg samples. The DTA was also taken on a Stanton-Redcroft DTA-671 (only up to 450°C due to the limitations of the instrument) using button-shaped platinum crucibles and taking 5–10 mg samples. Ignited alumina was used as reference material. The heating rate for both TG and DTA was 10°C min^{-1} and the studies were carried out in an atmosphere of static air. Isothermal studies were carried out in a muffle furnace fitted with a pyrometer and temperature controller. 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 diffraction patterns were taken on a Philips diffractometer using CuK_α radiation. Both AMO and PMO are shown to be crystalline with a low symmetry class. Some of their d values are given in Table 1. The magnetic measurements were taken on a vibrating sample magnetometer model VSM-155 at room temperature (23°C) and at the liquid nitrogen temperature, using a magnetic field of 5500 Gauss.

RESULTS AND DISCUSSION

Like other molybdenum(VI) compounds [4–6], both AMO and PMO show a small amount of paramagnetism which is independent of temperature, their magnetic moments being 0.32 and 0.30 BM, respectively. The IR spectra of both AMO (Fig. 1A) and PMO (Fig. 2A) show the bands of the coordinated oxalato group and these have been assigned on the basis of existing data in the literature [7,8]. The probable assignments are given in Table 2. AMO shows two additional strong bands at about 3200 and 1400 cm^{-1}. 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 [9]. In addition to this, AMO shows strong absorption

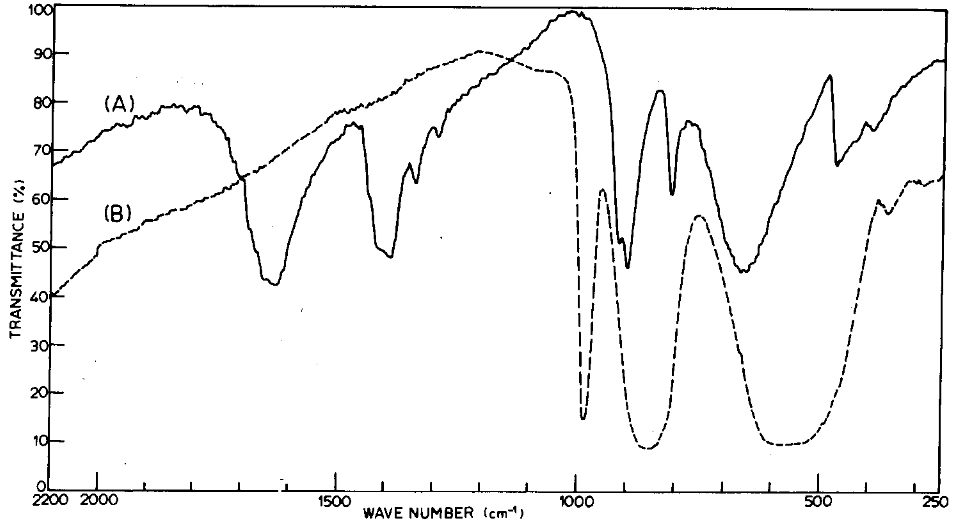

Fig. 1. IR spectra of (A) AMO and (B) AMO heated to 325°C.

bands at about 920, 900 and 660 cm^{-1} while PMO shows similar bands at 930, 910 and 660 cm^{-1}, the band around 660 cm^{-1} being broad in each case. The two strong bands in the 900 cm^{-1} region suggest the presence of metal–oxygen double bonds [10,11]. These bands may be assigned to asymmetric and symmetric Mo=O stretches [12]. The broad band at 660 cm^{-1} is similar to one which is observed in the IR spectrum of MoO_3, and accordingly it may be assigned to the O–Mo–O stretch.

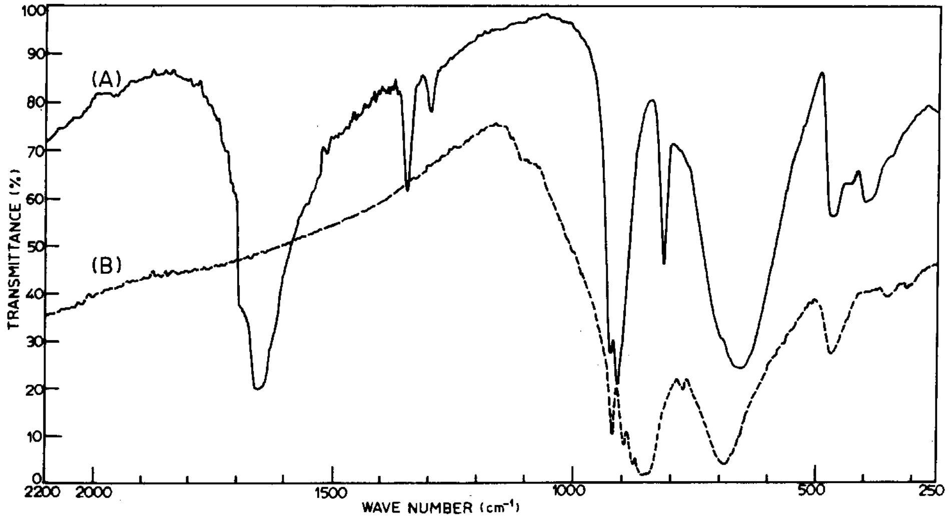

Fig. 2. IR spectra of (A) PMO and (B) PMO heated to 500°C.

TABLE 2

IR absorption bands of AMO and PMO and their probable assignments

Frequency (cm^{-1})		
AMO	PMO	Probable assignment
1660 vs	1660 vs	νas (C=O)
3200 s,br		νas (NH_4^+)
1400 vs,br		δ (NH_4^+)
1340 s 1295 s	1350 vs 1305 s	νsym(C–O) + δ(O–C=O)
920 s	930 s	νas MO=O
900 s	910 s	νsym Mo=O
810 s	820 s	ν(O–C=O) + ν(M–O)
660 s,br	660 s,br	ν(O–Mo–O)
485 w	485 w	ring def. + δ(O–C=O)
440 w	440 w	ν(M–O) + ring def.

vs = Very strong, s = strong, w = weak, br = broad.
as = Asymmetric; sym = symmetric.

Figure 3 gives the DTA, TG and differential thermogravimetric (DTG) curves for AMO in an atmosphere of static air. The thermogram shows that AMO contains no water molecule and it is stable up to 255°C. The decomposition of oxalate accompanied by the evolution of ammonia starts at 255°C and extends up to 320°C to give the end product MoO_3 in a single step. The peak corresponding to this reaction is observed in DTG at about 305°C. The two DTA curves taken on two different instruments, DTA 673-4 (Fig. 3, DTA-1) and DTA-671 (Fig. 3, DTA-2), differ in that in the former the endothermic peak due to the decomposition of oxalate at about 315°C is immediately followed by a broad exotherm at about 340°C, for which there is no corresponding weight loss on the TG curve; in the latter the decomposition of AMO is observed as a single endothermic peak around 310°C. This difference may be attributed to the different geometry of the crucibles and design of the furnace in the two instruments, DTA-671 probably allowing an easier escape of the gases evolved during decomposition. The exothermic peak observed in the DTA-1 curve may be due to the oxidation of lower oxides of molybdenum formed during the primary decomposition process. It appears that the reducing atmosphere created by the evolved carbon monoxide, and particularly ammonia [13], causes a reduction of the metal ion probably from molybdenum(VI) to molybdenum(V). Similar behaviour has been observed during the decomposition of $(NH_4)_2$-$[MoO_3(C_2O_4)] \cdot H_2O$ [2]. Such a reduction of the metal ion has also been reported during the decomposition of other oxalato compounds [14,15]. As seen on the TG curve, a 100% weight loss is obtained between 700 and 830°C which corresponds to the complete sublimation of MoO_3. This is

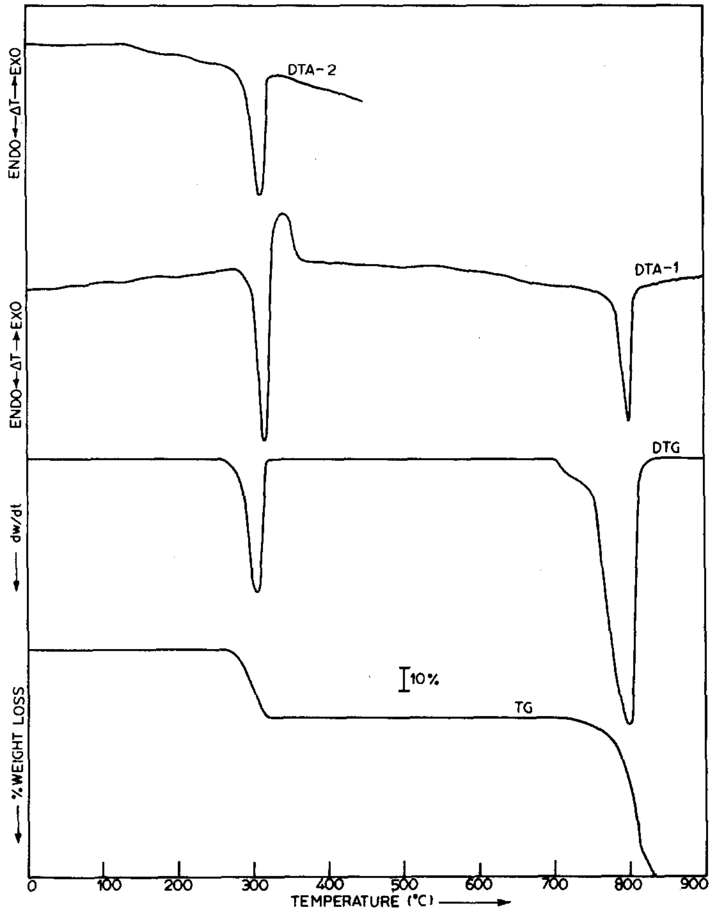

Fig. 3. DTA, TG and DTG of AMO in air.

observed in DTG as a peak around 800°C. DTA-1 also shows an endothermic peak at about 800°C which may be attributed to the sublimation accompanied by the melting (melting point of MoO_3 being 795°C) of MoO_3. The observed weight loss for the process

$$(NH4)_2[Mo_2O_6(C_2O_4)] \rightarrow 2\ MoO_3$$

is 30.07% while the calculated value is 30.10%.

AMO was heated isothermally at 325°C and the product was characterized by IR and X-ray diffraction studies. These reveal the formation of pure MoO_3. Table 3 gives a comparison of the observed *d* values with the earlier reported data for MoO_3 [16]. The IR spectrum of the end product is also identical to that of MoO_3 [17].

Figure 4 gives the DTA, TG and DTG curves for PMO in an atmosphere of static air. As seen on the TG curve, PMO is also an anhydrous compound

TABLE 3

d Values (Å) for MoO_3 and $K_2Mo_2O_7$

Observed	Reported	Observed	Reported
6.931	6.93	7.09	7.10
3.809	3.81	6.91	6.93
3.460	3.463	5.979	5.98
3.26	3.26	5.218	5.22
3.005	3.006	4.92	4.92
2.701	2.702	4.80	4.81
2.653	2.655	3.858	3.86
2.528	2.527	3.671	3.67
2.33	2.332	3.468	3.47
2.31	2.309	3.33	3.33
2.27	2.271	3.302	3.30
2.133	2.131	3.268	3.27
1.979	1.982	3.189	3.19
1.959	1.960	3.118	3.12
1.850	1.849	3.07	3.07
1.82	1.821	2.964	2.966
1.73	1.733	2.944	2.945
1.69	1.693	2.878	2.880
1.662	1.663	2.610	2.616
1.632	1.631	2.478	2.478
1.594	1.597	2.193	2.199
1.567	1.569	2.146	2.149
1.478	1.477	2.078	2.080
1.442	1.443	2.003	2.004
1.432	1.435	1.876	1.879

and is stable up to 300°C. The decomposition of oxalate starts at 300°C and extends to about 380°C to give the end product $K_2Mo_2O_7$ in a single step. This is observed in DTG as a peak at about 355°C. The DTA of PMO was also taken on the two instruments DTA 673-4 (Fig. 4, DTA-1) and DTA-671 (Fig. 4, DTA-2). Again the two curves differ in that in the DTA-1 curve the endothermic peak due to the decomposition of oxalate at about 355°C is immediately followed by a sharp exothermic peak at about 360°C, while the DTA-2 curve represents the decomposition of oxalate as a single endothermic peak at about 350°C. The exothermic peak in the DTA-1 curve may be due to the domination of oxidation of carbon monoxide liberated during decomposition, thus both these peaks represent the decomposition of oxalate. The absence of such a peak in the DTA-2 curve may again be attributed to the different geometry and the design of the furnace of the DTA-671 instrument which probably allows an easier escape of the gases evolved during decomposition. The total observed weight loss for the process

$$K_2[Mo_2O_6(C_2O_4)] \rightarrow K_2Mo_2O_7$$

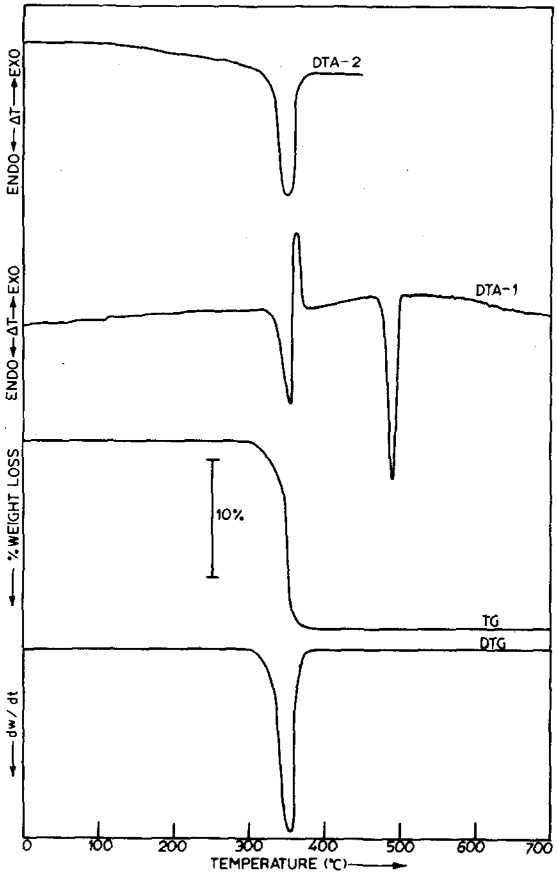

Fig. 4. DTA, TG and DTG of PMO in air.

is 15.81% compared with the calculated value of 15.85%. An additional endothermic peak is observed in the DTA-1 curve at about 490°C, for which no corresponding weight change is observed on the TG curve. Thus this peak may be due to some physical change and it has been attributed to the melting of the end product. On heating isothermally at 500 ± 5°C, the sample gives a molten product which immediately solidifies to a white crystalline compound, confirming that the peak at 490°C is due to melting.

The end product was characterized by chemical analysis of the solidified molten product obtained by heating PMO isothermally at 500°C as well as at 400°C. Both these products gave identical chemical analysis, IR (Fig. 2B) and X-ray diffraction patterns. The IR absorption bands are similar to those reported for $Na_2Mo_2O_7$ [18]. The X-ray pattern reveals the formation of pure $K_2Mo_2O_7$ without any other phase. Table 3 shows that the observed *d* values closely match with the earlier reported data [19].

The above results and discussions based on TG and other data allow us to propose eqns. (1) and (2) to represent the thermal decomposition of AMO and PMO, respectively

$$(NH_4)_2[Mo_2O_6(C_2O_4)] \overset{255-320°C}{\rightarrow} 2\,MoO_3 + 2\,NH_3 + CO + CO_2 + H_2O \quad (1)$$

$$K_2[Mo_2O_6(C_2O_4)] \overset{300-380°C}{\rightarrow} K_2Mo_2O_7 + CO + CO_2 \quad (2)$$

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