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INVESTIGATION ON THE FORMATION OF POTASSIUM TRIMOLYBDATE VIA THERMAL DECOMPOSITION OF A NEW OXOMOLYBDENUM(VI) OXALATO COMPLEX

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The complex $K_4(NH_4)_2$ $[Mo_6O_{15}(C_2O_4)_6(H_2O)_4]$ (PAMO) was prepared and characterized on the basis of chemical analysis and IR spectral data. Its thermal decomposition was studied by using TG and DTA techniques. PAMO loses its water between 190 and 225°C followed by the decomposition of anhydrous PAMO, which takes place in three stages. The first two stages occur in the temperature ranges 225-245°C and 245-270°C, to give the intermediates with tentative compositions $K_{12}(NH_4)_2$ $[Mo_{18}O_{45}(CO_3)_4(C_2O_4)_{12}]$ and $K_{12}[Mo_{18}O_{54}(CO_3)_2(C_2O_4)_4]$ respectively, the latter then decomposing in the third stage between 270 and 335°C to give the end product, potassium trimolybadate ($K_2Mo_3O_{10}$). The end product was characterized by chemical analysis, IR spectral and X-ray studies.

A survey of literature reveals that although some lower molybdates [1, 2] have been prepared by the thermal decomposition of some oxomolybdenum(VI) oxalato complexes, but the preparation of higher molybdates by the pyrolysis of precursor compounds have received scant attention. The present work deals with the preparation, characterization and thermal decomposition of a new oxomolybdenum(VI) oxalato complex, $K_4(NH_4)_2$ $[Mo_6O_{15}(C_2O_4)_6(H_2O)_4]$ which gives potassium trimolybdate ($K_2Mo_3O_{10}$) as the end product.

Experimental

Baker analysed ammonium para-molybdate and Analar grade of potassium chloride, ammonium chloride and oxalic acid were used to prepare

PAMO as follows: To a hot solution of 3.7815 gms of oxalic acid in about 250 ml of distilled water, 4.3185 gms of molybdenum trioxide (prepared by heating ammonium para-molybdate at about 400° for 2h) was added in small lots and the solution was filtered to remove any unreacted molybdenum trioxide. To this 1.4912 gms of potassium chloride and 0.535 gms of ammonium chloride were added and the solution was concentrated to about 30 ml to obtain crystals of PAMO, which were washed with distilled water and 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 [3] and potassium was estimated by flame photometric method. The analysis of PAMO gave: NH_4^+, 2.23%; K^+, 9.72%; Mo, 35.77% and $C_2O_4^{2-}$, 32.84% the calculated values being 2.24%, 9.72%, 35.79% and 32.83% respectively. These data show that there is no noticeable deviation of PAMO from the composition $K_4(NH_4)_2[Mo_6O_{15}(C_2O_4)_6(H_2O)_4]$.

Thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) were carried out on a Stanton Redcroft thermoanalyzer model STA-780 series taking 10-20 mg of the samples in platinum crucibles. For DTA, ignited alumina was used as the reference material. The heating rate was 10 deg/min. 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_α radiations. Magnetic measurements were made on a vibrating sample magnetometer model VSM-155 at room temperature (23°), using a magnetic field of 5500 Gauss.

Results and discussion

PAMO is a white powder and its X-ray diffration pattern reveals that it is a crystalline compound probably with a low symmetry. The magnetic measurements indicate it to be diamagnetic, suggesting that it is a molybdenum(VI) complex [4]. 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 this, the broad band at 3200 cm^{-1} probably results from NH_4^+, asymmetric stretching vibrations and the band at 1410 cm^{-1} is probably due to NH_4^+, bending vibrations [7]. The two strong bands at 940 and 910 cm^{-1} suggest the presence of metal oxygen double bonds and the bands at 840 and 650 cm^{-1} can be assigned to the asymmetric and symmetric Mo-O stretches respectively [8-10]. In addition to these, three weak bands have also been observed at 900, 770 and 680 cm^{-1}, which are probably due to the rocking, wagging and metal oxygen stretching vibrations, respectively, of the coordinated water [11].

Figure 2 gives the DTA, TG and DTG curves for PAMO in an atmosphere of static air. The thermoanalytical curves show that the dehydration of PAMO takes place in a single step and is immediately followed by the decomposition of anhydrous PAMO, which is a multistep process. The various stages are discussed in detail below.

Table 1 IR absorption bands of PAMO and their probable assigments

Frequency, cm^{-1}	Band Position	Probable Assignment
3500	s, br	ν(OH)
3200	s, br	νas (NH$_4^+$)
1660	vs, br	νas (C=O)
1410	vs	δ (NH$_4^+$)
1340	s	νsym (C-O)+δ(O-C=O)
1300	s	
940	s	νas Mo=O
910	s	νsym Mo=O
900	w	Coordinated Water
840	s	ν (O-Mo-O)
790	m	δ(O-C=O)+ν (M-O)
770	w	Coordinated Water
680	w	Coordinated Water
650	s, br	ν (O-Mo-O)
470	m	ring def.+δ(O-C=O)
430	w	ν (M-O)+ring def.
415	m	δ(O-C=O)

vs = Very strong, s = Strong, m = Medium, w = Weak, br = Broad, as = Asymmetric, sym = Symmetric

Dehydration

PAMO is stable up to 190° and then loses its four moles of water in a single step between 190 and 225°. This is observed in DTA and DTG as peaks at 210 and 215° respectively. The observed weight loss is 4.46%, the calculated value being 4.48%. The loss of water at such a high temperature indicates that water molecules are probably coordinated to the metal.

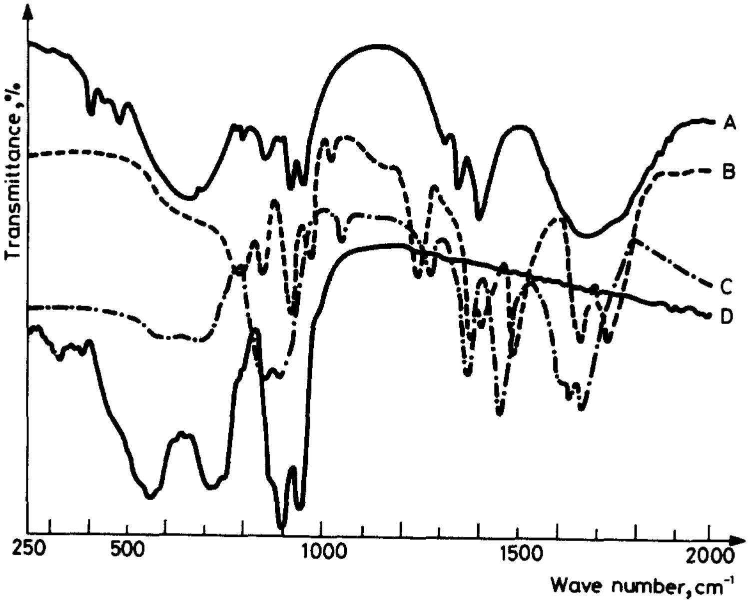

Fig. 1 IR spectra of PAMO (A), PAMO heated at 245°C (B), 270°C (C) and 340°C (D)

Decomposition

As seen on the TG curve, the dehydration of PAMO is immediately followed by the decomposition of the anhydrous compound, which occurs in three stages between 225 and 335°. The first stage extends up to 245° and corresponds to the loss of four moles of ammonia, two moles of water, six moles of carbon monoxide and two moles of carbon dioxide per three moles of PAMO, to give an intermediate compound with the tentative composition $K_{12}(NH_4)_2$ $[Mo_{18}O_{45}(CO_3)_4(C_2O_4)_{12}]$. This is seen in DTG as peak at 240°. However in DTA, an endothermic peak at 240° is immediately followed by a sharp exothermic peak at 245° which may be due to the domination of the evolved carbon monoxide into carbon dioxide. The observed weight loss is 7.45%, against the calculated value of 7.47%. The second stage occurs between 245 and 270° and involves a further loss of two moles of ammonia, one mole of water, eight moles of carbon monoxide and ten moles of carbon dioxide to give another intermediate having the tentative composition

$K_{12}[Mo_{18}O_{54}(CO_3)_2(C_2O_4)_4]$. This stage is observed in DTG as peak at 265°C. However, DTA shows a small endothermic peak at 260° followed by a sharp exothermic peak at 265°, which may again be due to the domination of the oxidation of carbon monoxide into carbon dioxide. The observed weight loss is 14.82% against the calculated value of 14.84%. The third and last stage occurs between 270 and 335° and involves the decomposition of $K_{12}[Mo_{18}O_{54}(CO_3)_2(C_2O_4)_4]$ to give the end product $K_2Mo_3O_{10}$. This is observed in DTG and DTA as peaks at 285 and 290° respectively. The observed weight loss is 7.77% as compared to the calculated value being 7.79%. The total weight loss observed for the process $K_4(NH_4)_2[Mo_6O_{15}(C_2O_4)_6(H_2O)_4] \rightarrow 2K_2Mo_3O_{10}$ is 34.50% compared with the calculated value of 34.58%.

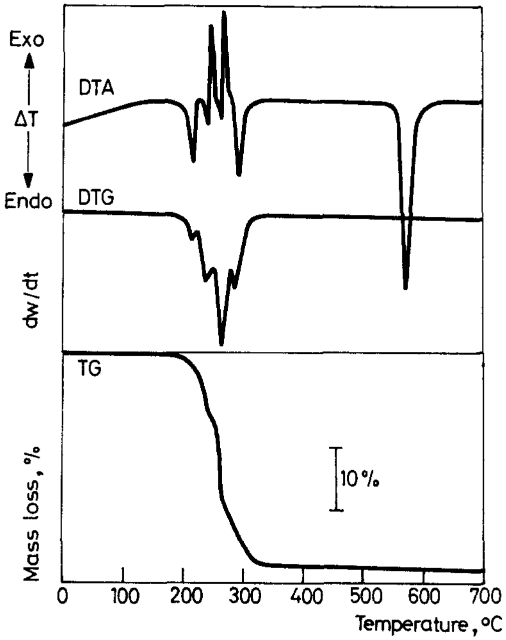

Fig. 2 TG, DTG and DTA curves of PAMO

The compositions assigned to the intermediates on the weight loss basis were further confirmed by chemical analysis, magnetic measurements and IR spectral studies. PAMO was isothermally heated at 245 ±5° and at

270±5° and the two samples were chemically analysed for K^+, NH_4^+, $C_2O_4^{2-}$ CO_3^{2-} and Mo. The experimental data were found to be in good agreement with the calculated values. Both these samples were found to be diamagnetic suggesting that they are molybdenum(VI) complexes [4]. In addition to the bands characteristic of oxalate and carbonate [5, 12] groups in the IR spectra of the two samples (Fig. 1B and 1C respectively), the IR spectrum of the sample obtained at 245 ±5° also shows two strong bands at 3200 and 1400 cm^{-1} indicating the presence of NH_4^+.

Melting

DTA shows an additional endothermic peak at 570°, corresponding to which no weight change is observed on the TG curve. This has been attributed to the melting of the end product, the reported melting point of $K_2Mo_3O_{10}$ also being the same [13]. On heating PAMO isothermally at 575±5°, a molten product was obtained, which immediately solidified to a white crystalline compound, then confirming the peak at 570° to be due to the melting of the end product.

The end product was obtained by heating PAMO isothermally at 340 as well as at 575°. The two samples gave identical chemical analysis, IR spectra (Fig. 1D), and X-ray diffraction patterns. These observations reveal the formation of pure $K_2Mo_3O_{10}$ without any other phase. The observed 'd' values closely match the earlier reported data [14]. The IR spectrum is also identical to that reported in the literature [15]. On the basis of all these studies. the following tentative scheme may be proposed for the thermal decomposition of PAMO in air

$$K_4(NH_4)_2[Mo_6O_{15}(C_2O_4)_6(H_2O)_4] \xrightarrow{190-225^\circ}$$

$$K_4(NH_4)_2[Mo_6O_{15}(C_2O_4)_6] + 4H_2O \qquad (1)$$

$$3K_4(NH_4)_2[Mo_6O_{15}(C_2O_4)_6] \xrightarrow{225-245^\circ}$$

$$K_{12}(NH_4)_2[Mo_{18}O_{45}(CO_3)_4(C_2O_4)_{12}] + 4NH_3 + 2H_2O + 6CO + 2CO_2 \qquad (2)$$

$$K_4(NH_4)_2[Mo_{18}O_{45}(CO_3)_4(C_2O_4)_{12}] \xrightarrow{245-270^\circ}$$

$$K_{12}[Mo_{18}O_{54}(CO_3)_2(C_2O_4)_4] + 2NH_3 + H_2O + 8CO + 10CO_2 \qquad (3)$$

$$K_{12}[Mo_{18}O_{54}(CO_3)_2(C_2O_4)_4] \xrightarrow{270-335^\circ}$$

$$6K_2Mo_3O_{10} + 4CO + 6CO_2 \qquad (4)$$

Equation (1) represents the dehydration of PAMO, while equation (2), (3) and (4) represents the three different stages of decomposition of anhydrous PAMO to give the end product. The mechanism proposed here is a tentative one based on the results obtained from dynamic thermogravimetry and isothermal studies.

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Zusammenfassung — Die Komplexverbindung $K_4(NH_4)_2[Mo_6O_{15}(C_2O_4)_6(H_2O)_4]$ (PAMO) wurde hergestellt und auf der Basis von chemischer Analyse und IR-Spektrum characterisiert. Mittels TG und DT Techniken wurde die thermische Zersetzung untersucht. Zwischen 190 und 225°C gibt PAMO alles Wasser ab, anschlieend erfolgt in drei Schritten eine

Zersetzung des dehydratierten PAMO. Die ersten zwei Schritte verlaufen in den Temperaturbereichen 225 - 245°C bzw. 245-270°C und liefern Zwischenprodukte der Zusammensetzung $K_{12}(NH_4)_2[Mo_{18}O_{45}(CO_3)_4(C_2O_4)_{12}]$ bzw. $K_{12}[Mo_{18}O_{54}(CO_3)_2(C_2O_4]$. Letzteres zerfällt dann in einem dritten Schritt zwischen 270 und 335°C und liefert Kaliumtrimolybdat ($K_2Mo_3O_{10}$) als Endprodukt, welches mittels Elementaranalyse, IR- und Röntgendiffraktionsuntersuchungen