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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 $A_2[MoO_3(C_2O_4)] \cdot H_2O$ where $A = K^+$ or NH_4^+ are prepared, characterized by chemical analysis and infrared spectra and their thermal decomposition studied by DTA and TGA. A chain structure containing MoO_6 octahedra linked through oxygen is proposed for the complex oxalates on the basis of i.r. absorption spectra. The ammonium compound decomposes endothermally around 270°C to give lower oxides of molybdenum which are finally oxidised to MoO_3, while the final decomposition product of the potassium compound is K_2MoO_4.

MOLYBDENUM(VI) forms a variety of anionic oxomolybdenum oxalates of which the following compounds have been characterized[1]: $NaNH_4[MoO_3(C_2O_4)] \cdot 2H_2O$, $K_2[Mo_2O_5(C_2O_4)_2] \cdot 2H_2O$, and $(Quin\ H)_2[MoO_2(C_2O_4)_2]$. The crystal structure of the first two compounds has recently been determined by X-ray diffraction method[2, 3]. It seems that the type of anionic molybdenyl oxalate formed, depends upon, among other factors, the size of the cation. In this note, the preparation, characterization and thermal decomposition of oxalates of the type $A_2[MoO_3(C_2O_4)] \cdot H_2O$ where $A = K^+$ or NH_4^+ are reported.

EXPERIMENTAL

High purity molybdic acid (Baker Analysed) was heated to about 200°C to obtain MoO_3. Analar grade ammonium oxalate, potassium oxalate and oxalic acid were employed in the preparation of the compounds.

Preparation. To a hot solution of 2·75g of potassium oxalate and about 1·0g of oxalic acid in 50 ml of water, 2·9g of MoO_3 were added in small lots. The solution was filtered to remove any unreacted MoO_3 and the clear solution concentrated to get crystals of the complex oxalate.

The ammonium molybdenyl oxalate was prepared by the same procedure employing ammonium oxalate as the starting material.

Both the compounds are white crystalline solids soluble in water.

Analyses. Molybdenum in the compounds was determined gravimetrically as molybdenyl oxinate and oxalate by $KMnO_4$ oxidation. The potassium content in the potassium compound was estimated by flame photometric method. The results of the analyses are presented in Table 1.

The thermogravimetric study of the compounds in air was carried out on a Stanton thermobalance, model HT-SM, with a heating rate of 6° per minute, while the differential thermal analysis (DTA) in air was done using a manual apparatus employing chromel–alumel thermocouples. The heating rate was around 8° per minute. Ignited alumina was used as the reference material. The i.r. spectrum of the compounds in KBr disc was recorded with a Carl–Zeiss UR10 spectrophotometer.

1. P. C. H. Mitchell, *Q. Rev. chem. Soc.*, **20**, 103 (1966).
2. F. A. Cotton, S. M. Morehouse and J. S. Wood, *Inorg. Chem.* **3**, 1603 (1964).
3. L. O. Atomovniyan and G. B. Bokii, *Zh. strukt. Khim.* **4**, 576 (1963).

Table 1. Results of the analyses of the compounds

Compound	Found % Mo	$C_2O_4^{2-}$	K^+	Calc. % Mo	$C_2O_4^{2-}$	K^+
$(NH_4)_2[MoO_3C_2O_4] \cdot H_2O$	33·25	30·68		33·55	30·77	
$K_2[MoO_3C_2O_4] \cdot H_2O$	28·84	26·76	24·10	29·23	26·81	23·83

RESULTS AND DISCUSSION

I.R. spectra and the structure of the compounds

The i.r. spectrum of both the compounds has been found to be essentially similar except for the presence of bands due to ammonium ion in the ammonium compound. An assignment of the important i.r. absorption frequencies of the compounds are given in Table 2. Besides the absorption bands due to the coordin-

Table 2. I.R. absorption bands of $K_2[MoO_3C_2O_4] \cdot H_2O$ and their probable assignments*

Frequency (cm^{-1})	Assignment
3500 s, br	ν(OH) of uncoordinated water
1680 vs	ν_a(C═O)
1460 s	ν_{sym}(C═O)
1300 s	ν_{sym}(C—O)
910 m	ν(C—C) + $\nu(MoO_2)_t$
885 s	$\nu(MoO_2)_t$
730 s, br	ν(—O—Mo—O)
790 m	δ_a(O—C—O)
530 w	δ_{sym}(C—C—O)
480 w	δ_{sym}(O—C—O)

*s = strong, br = broad, m = medium, w = weak, vs = very strong, ν = stretch, a = asymmetric, sym = symmetric, t = terminal, δ = bending.

ated oxalato group, the compounds show fairly strong bands at 910,885 and 730 cm^{-1}, the latter being slightly broader. In oxomolybdenum(VI) compounds containing both bridged and terminal oxygen atoms directly attached to molybdenum, more than one metal–oxygen stretching bands have been observed[1, 4]. As an example, the complex oxalate $K_2[Mo_2O_5(C_2O_4)_2] \cdot (H_2O)_2$ shows Mo–O stretch at 960, 920 and 860 cm^{-1}[4a]. In the present instance also the bands observed at 910, 885 and 730 cm^{-1} can be attributed to Mo–O stretch. This would reveal that both the compounds contain terminal and bridged Mo–O groups. The crystal structure of $NaNH_4[MoO_3C_2O_4] \cdot 2H_2O$, a compound quite similar to those described here, has been determined by X-ray diffraction[3]. The crystal

4a. F. A. Cotton and R. M. Wing, *Inorg. Chem.* **4**, 867 (1965).
4b. M. Cousins and M. L. H. Green, *J. chem. Soc.* 1567 (1964).

structure consists of an infinite chain of MoO_6 octahedral linked through oxygen bridges containing cis-MoO_2 groups. The i.r. absorption data of the compounds discussed here are compatible with a similar structure, the absorption at 910 and 885 cm^{-1} being ascribed to the stretching of terminal cis-MoO_2 groups and the broad band at 730 cm^{-1} being due to the bridged -O-Mo-O- stretch. The ν(OH) of water occurs as a broad band around 3500 cm^{-1}, indicating that the water molecule is not coordinated to the metal.

Thermal behaviour of the compounds

The DTA and TGA curves of the ammonium and potassium compounds are presented in Figs. 1 and 2 respectively. The first endotherm obtained at 100° with the ammonium compound may be associated with the loss of water of hydration as

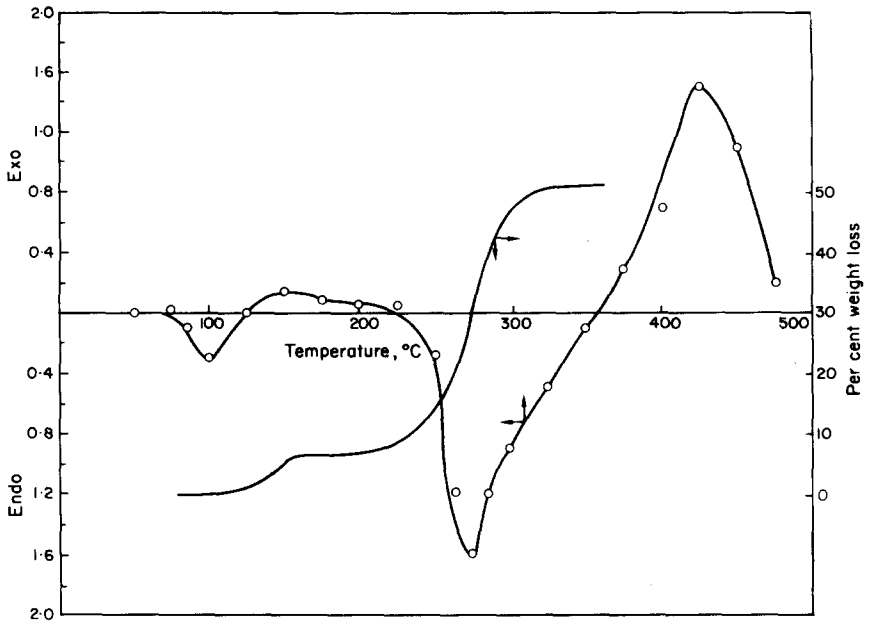

Fig. 1. DTA and TGA of $(NH_4)_2[MoO_3C_2O_4] \cdot H_2O$ in air.

borne out by the TGA curve. The anhydrous compound is stable up to 200°C beyond which the decomposition starts. The decomposition attains a maximum rate around 240°C, while the process is complete at 320°C as revealed by the weight loss curve. In the DTA curve, the decomposition is observed as an endothermic peak, centred around 270°C. This is followed by a sharp exotherm at about 400°C, corresponding to which no weight loss is observed in the TG curve. The sharp exothermic peak may be due to the oxidation of lower oxides of molybdenum formed during the primary decomposition process. This suggests that during the decomposition, the metal undergoes reduction from Mo(VI) to probably Mo(V). Such a reduction of the metal ion during the solid state decomposition of oxalates is not uncommon and it has been observed in the thermal decomposition of $(NH_4)_3$

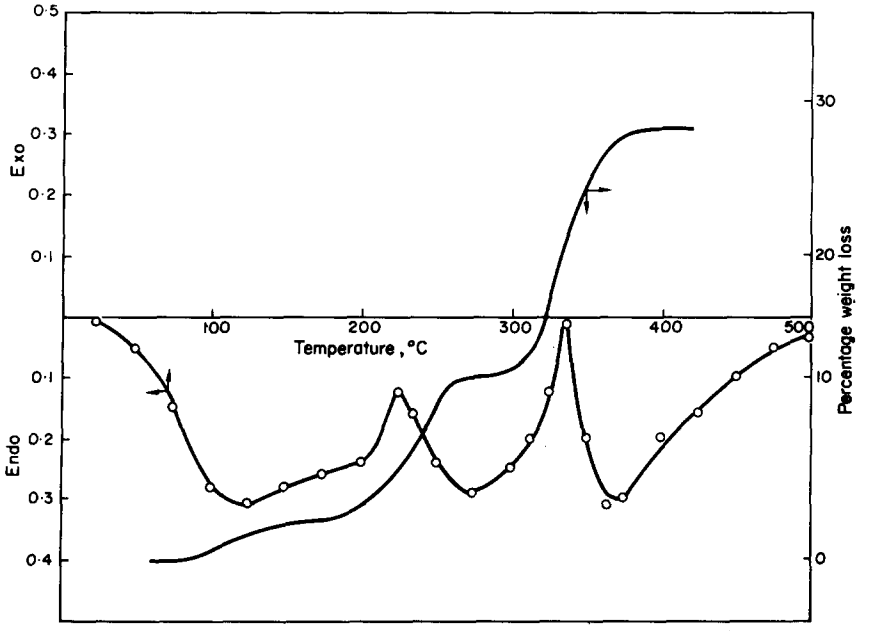

Fig. 2. DTA and TGA of $K_2[MoO_3C_2O_4] \cdot H_2O$ in air.

$[VO_2(C_2O_4)_2]$ where V(V) is reduced to V(IV)[5] and also in europium(III) oxalate[6]. That Mo(VI) undergoes reduction during the decomposition is also indicated by the formation of an intense blue product, which becomes colourless on further heating. However, the characterization of this intermediate is difficult as it is very unstable. The final product of decomposition is MoO_3 as analysed. The expected weight loss for the process

$$(NH_4)_2[MoO_3(C_2O_4)] \cdot H_2O \rightarrow MoO_3$$

is 49·65 per cent, while the experimental value as obtained from the thermogravimetric curve is 50·15 per cent. The final product has also been ascertained to be MoO_3 by X-ray powder diffraction.

The dehydration of the potassium compound starts from 100°C and proceeds beyond 200°C. The anhydrous compound in this case is not stable but the endothermic decomposition of the compound starts immediately after the dehydration and proceeds in two stages, as shown by the DTA curve (Fig. 2.). The total weight loss corresponds to the formation of the final product K_2MoO_4 (Calculated weight loss: 27·43; experimental: 28·06%) as also confirmed by chemical analysis.

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6. A. Glasner, E. Levy and M. Steinberg, *J. inorg. nucl. Chem.* **25**, 1415 (1963).