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THE THERMAL DECOMPOSITION OF OXALATES. PART 21. THE PREPARATION AND THERMAL DECOMPOSITION OF AN OXY MOLYBDENUM(VI) OXALATE

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ABSTRACT

The complex oxomolybdenum(VI) oxalate having the formula $MoO_2C_2O_4 \cdot 2H_2O$ has been prepared and characterized by chemical analysis and infrared spectra and its thermal decomposition has been studied by TG and DSC. The molybdenum oxalate prepared decomposes exothermally between 200 and 300°C in one step. The product of this decomposition is molybdenum oxide, (blue oxide); this compound has been characterized by X-ray powder diffraction and the observed *d* values are identical with data reported for MoO_3.

INTRODUCTION

Interest in the study of inorganic oxalates has resulted largely from the use of oxalates in analytical chemistry and industry.

The technological importance of mixed oxides has attracted the attention of chemists and ceramicists leading to their preparation by simpler methods and to products of high purity. One such procedure is the thermal decomposition of precursor oxalates [1]. In this study the preparation and thermal analysis of molybdenum oxalate is described.

Molybdenum(III) and molybdenum(IV) oxalate complexes were prepared previously by Wardlaw [2–4] and recently by Benory et al. [5]. Wardlaw described the preparation of $Mo_2O(C_2O_4)_2 \cdot 6H_2O$, $Mo_4O_3(C_2O_4)_3 \cdot 12H_2O$, $Mo(OH)(C_2O_4) \cdot 3H_2O$, $MoO(C_2O_4) \cdot 3H_2O$ and discussed their chemical reactivity and structural similarities to Cr(III) oxooxalates and Mo(III) oxosulphates.

Molybdenum(VI) forms a variety of anionic oxomolybdenum oxalates [6–11]. In a previous paper we described the preparation of oxalates of molybdenum by different reaction routes and their decomposition [12].

The present work deals with the preparation, characterization and thermal decomposition of a molybdenum(VI) oxalate complex having the formula $MoO_2(C_2O_4)\cdot 2H_2O$; this compound gives MoO_3 as the end product.

EXPERIMENTAL

Molybdenum(II) acetate dimer was reacted with oxalic acid dihydrate as follows. Oxalic acid was dissolved in methanol. Solid molybdenum(II) acetate dimer was initially added a little at a time, but a red precipitate appeared and continued to be produced as the rest of the acetate was added; the solution was dried in vacuum. The molar ratio of molybdenum acetate to oxalic acid was 2 : 3.

Molybdenum in the compound was determined gravimetrically as molybdenyl oxinate [13] and oxalate by titration with potassium permanganate [14]. The analysis gave: Mo, 37.50% and $C_2O_4^{2-}$, 34.10%, whereas the calculated values are: Mo, 38.1% and $C_2O_4^{2-}$, 35% based on the formula $MoO_2\ (C_2O_4)\cdot 2H_2O$ (Table 1).

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on an Omnitherm thermal analysis system. Samples of less than 10 mg were used for TG and the heating rate was 10°C min^{-1}. For DSC, about 2 mg samples were used and the heating rate was 5°C min^{-1}. Both studies were carried out in a dynamic atmosphere of air and nitrogen. The flow rate was 25 ml min^{-1}.

The product of the first decomposition was analyzed by X-ray powder diffraction. A KBr matrix was prepared containing this oxalate. The mass ratio of oxalate to KBr was 1 : 20. This oxalate was examined using a diffuse reflectance infrared fourier transform (DRIFT) technique in the range 400–4600 cm^{-1}.

TABLE 1

TG data in N_2, at 10°C min^{-1}, flow rate 25 ml min^{-1}

Total % mass loss	Temperature range	Theoretical %
44.24 (dehydration and decomposition overlap)	Ambient to 320°C	14.28 for dehydration +28.57% for decomposition ≡ 42.85% overall
Plateau for "Blue" oxide	320–700°C	
Sublimation and melting occurred beyond 700°C		

Formula mass of oxalate (experimental) = 251.05.
Formula mass for $MoO_2(C_2O_4)\cdot 2H_2O = 252.00$.

RESULTS AND DISCUSSION

The results of the fourier transform infrared spectra (FTIR) obtained (Fig. 1) show the bands of the coordinated oxalate group and these have been assigned on the basis of data found in the literature [15,16]. The probable assignments are given in Table 2.

The band due to the hydroxyl of water occurs as a broad band around 3500 cm^{-1}, indicating that the water molecule is not coordinated to the

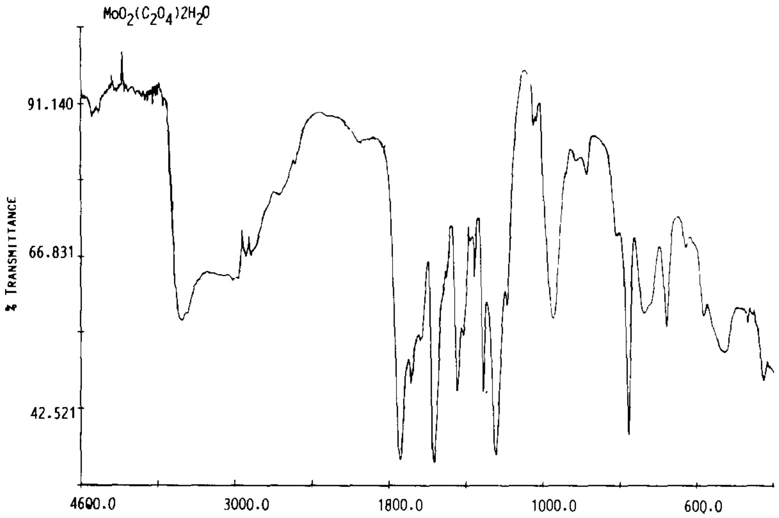

Fig. 1. FTIR spectra of molybdenum oxalate.

TABLE 2

FTIR data on molybdenum oxalate

Band position (cm^{-1})	Probable assignment
3580 S, br	$\nu(OH)$
1740 VS	$\nu_{as}C{=}O$
1700	$\nu_{as}C{=}O$
1570 VS	$\nu_{as}C{=}O$
1450 M	$\nu_s(C{=}O) + \nu(C{-}C)$
1370 W	$\nu_s(C{-}O) + \nu(C{-}C)$
1325 M	$\nu_s(C{-}O) + \delta(O{-}C{=}O)$
1240 S	$\nu_s(C{-}O) + \delta(O{-}C{=}O)$
975 S	Mo=O
780 S	-O-Mo-O-
740 M	-O-Mo-O-
680 M	-O-Mo-O-
530 M	$\nu(M{-}O) + \nu(C{-}C)$

VS = very strong, S = strong, M = medium, W = weak, br = broad, s = symmetric, as = asymmetric.

metal. Besides the absorption bands due to the coordinated oxalato group, the compound shows fairly strong bands at 975, 780, 740 and 680 cm^{-1}. In oxomolybdenum(VI) compounds containing both bridged and terminal oxygen atoms directly attached to molybdenum, more than one metal–oxygen stretching band has been observed [7]. In the present work the bands observed above can be attributed to a metal–oxygen (M–O) stretch. This reveals that the compound contains terminal and bridged M–O groups, so the absorption at 975 cm^{-1} can be ascribed to the stretching of the terminal *cis*-MO_2 group and the bands at 780, 740 and 680 cm^{-1} are due to the bridged –O–Mo–O– stretch. When a band is observed in the 900–1100 cm^{-1} region, it is good evidence for the existence of a metal=oxygen link, provided that there is no other atom (e.g. nitrogen) present in the molecule of similar atomic weight, which might give rise to a similar frequency [17].

THERMAL BEHAVIOR OF THE COMPOUND

The TG and DSC curves of the molybdenum oxalate are presented in Figs. 2 and 3 in dry nitrogen and dry air. In the DSC data the first endotherm obtained around 100 °C may be associated with the loss of water of hydration. The anhydrous compound is stable below 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 mass loss curve.

In the DSC curve, the decomposition is observed as an exothermic peak,

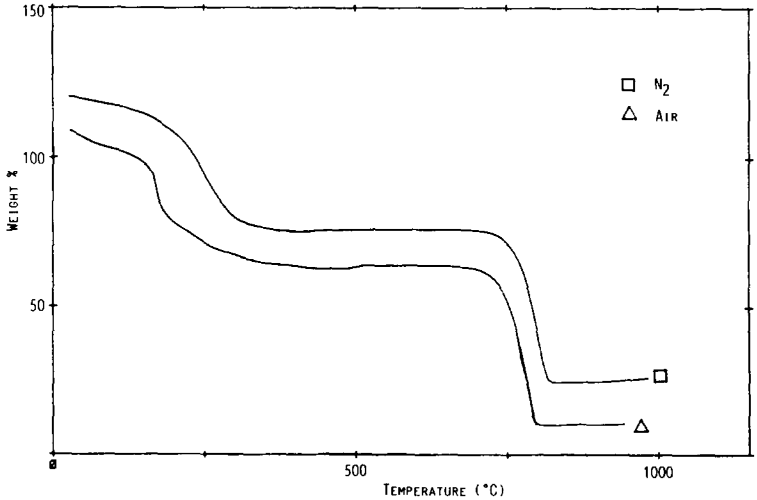

Fig. 2. TG curve of molybdenum oxalate. Note: the results in nitrogen and air have been displaced by 20 and 10%, respectively.

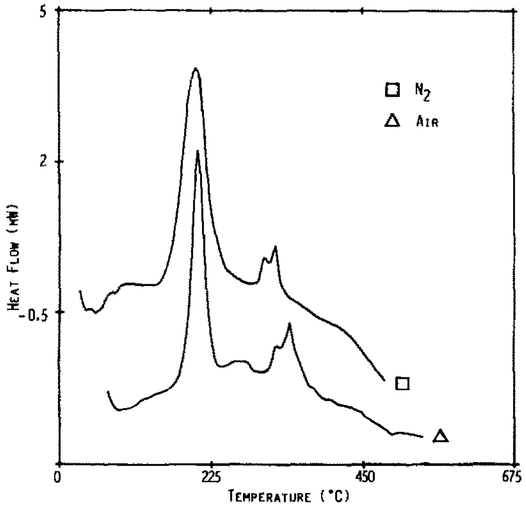

Fig. 3. DSC curve of molybdenum oxalate. Note: the result in air has been displaced by 3 mW and 50°C.

in both nitrogen and air, centered around 240°C. This followed by another exotherm at about 350°C, for which no appreciable mass loss is observed on the TG curve.

The exothermic decomposition peak in nitrogen is unusual for oxalates but not unique. Exothermic decompostions of mercuric [18], copper [19] and silver oxalates [20] have also been reported.

These decompositions are often described as autocatalytic but it is probable that in more environments the results are largely governed by the occurrence of self-heating. In the case of the molybdenum oxalate samples studied here it would seem likely that the first of these explanations is more plausible.

The second exothermic peak observed in the DSC curve appears to be a recrystallization phenomenon from an amorphous metastable state to a crystalline state. This is supported by the X-ray diffraction data which indicated an amorphous structure in the region immediately preceding the peak whereas the X-ray data on the sample which had undergone the exothermic change showed a good crystalline pattern for MoO_3, as shown in Table 3. A small mass change takes place just prior and possibly during the exothermic recrystallization. This could be loss of occluded gases but it could be due to the reducing atmosphere created by the evolved carbon monoxide causing a superficial reduction of the metal ion probably from molybdenum(VI) to molybdenum(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 $(NH_4)_2MoO_3C_2O_4 \cdot H_2O$, $(NH_4)_2\,Mo_2O_6(C_2O_4)$ [7,8] and $(NH_4)_3\,VO_2(C_2O_4)_2$ where V(V) is reduced

TABLE 3

X-ray data of MoO_3 ($\lambda = 1.5418$ Å, *d* values (Å) for MoO_3)

d values for sample prepared	I/I_0	*d* values reported [26]	I/I_0
6.945	S	6.93	34
3.810	VS	3.81	82
3.460	S	3.463	61
3.256	VS	3.260	100
3.016	W	3.006	13
2.699	W	2.702	19
2.653	M	2.655	35
2.529	W	2.527	12
2.331	W	2.332	12
2.304	M	2.309	31
2.271	W	2.271	18
2.119	W	2.131	9
2.027	W	1.996	4
1.982	W	1.982	13
1.961	W	1.960	17
1.848	M	1.849	21
1.821	W	1.821	11
1.787	W	1.771	5
1.733	W	1.733	17
1.695	W	1.693	8
1.663	W	1.663	13
1.637	W	1.631	13
1.598	W	1.597	15
1.570	W	1.569	16
1.501	W	1.504	5
1.443	W	1.443	12
1.431	W	1.435	12
1.386	W	1.386	5
1.352	W	1.352	6

VS = very strong, S = strong, M = medium, W = weak.

to V(IV) [21] and also in europium(III) oxalate [22], nickel [23], ferric [24] and plutonium [25].

The final product of decomposition shows a yellow color at high temperature, but this color disappears on cooling and becomes blue. This solid residue has been analyzed by X-ray powder diffraction. This reveals the formation of MoO_3. Table 3 gives a comparison of the observed *d* values with the reported data for MoO_3 [26].

According to the available literature this end product is not MoO_3 although it has the same basic structure, but it differs in the charges on cations and anions. The most plausible explanation offered for molybdenum blue is that the mean oxidation of Mo is between 5 and 6. The structure of molybdenum trioxide has been given by different workers [17,27]. It may be regarded as containing distorted MoO_6 octahedra in which three of the oxygen atoms are common to three MoO_6 octahedra, two of the oxygen atoms are common to two octahedra, and the sixth oxygen atom is unshared, i.e. bound to only one molybdenum atom. The non-stoichiometry of the oxide may be judged from an inspection of the TG curve. At 320°C the mass loss is 42.9%, corresponding to stoichiometric MoO_3 (but according to DSC, present in a disordered structure). The subsequent exothermic recrystallization produces a further small mass loss so that the total mass loss around 400°C when recrystallization has occurred is 44.24%. This indicates an oxide with formula $MoO_{2.92}$ which, although crystalline, has a non-stoichiometry of 1 oxygen in every 30 if a perfect structure of MoO_3 is assumed.

Finally, the sublimation of the MoO_3 begins at about 700°C and the melting point is at 795°C; because of this no residual material is in the holder at 1000°C.

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