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THE THERMAL DECOMPOSITION OF OXALATES. PART 22. THE PREPARATION AND THERMAL DECOMPOSITION OF SOME OXY TUNGSTEN(VI) OXALATES

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ABSTRACT

The preparation and characterization of tungsten oxalates are described. The compounds have been characterized on the basis of analytical and Fourier transform infrared (FTIR) spectral data. The thermal decomposition has been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). The tungsten oxalates prepared decompose endothermically between 100–250°C. The products of these decompositions have been characterized by X-ray powder diffraction as WO_3. The dehydration is usually seen as a separate degradation step distinct from the decomposition of the oxalate to the oxide. The composition of the oxalate precipitates varies with the method of preparation.

INTRODUCTION

Tungsten in the oxidation state (VI) forms a number of oxo compounds, some of which are oxalate complexes. The tungsten is reported as being incorporated with the oxalate ion to give cations $[WO_3(Ox)]^{2-}$ and $[W_2O_5(Ox)_3]^{4-}$ where Ox = oxalate ion [1]. This gives rise to reports on the preparation of $M^1_2[WO_2F_2(C_2O_4)]$ {where $M = K^+$, Rb^+, Cs^+, $1/3[Co(NH_3)_6]^{3+}$ and $1/3[Coen_3]^{3+}$}, $M^1_2[WO_2(C_2O_4)_2]$ {where $M = K^+$, Rb^+ and Cs^+}, $Rb_2[WO_3(C_2O_4)]$ [2]; $K_2[WO(O_2)_2(C_2O_4)]$ [3], and $[WO_2(C_2O_4)_2]^{2-}$ [4]. Here, the preparation, characterization, and thermal decomposition of oxalates of the type $WO_a(C_2O_4)_bcH_2O$, where $a = 2$ or 3, $b = 1$ or 3 and $c = 1$, 2, 4, or 6 are reported.

EXPERIMENTAL

Preparation

In this study, oxalates of tungsten have been prepared in various forms by different reaction routes. These routes can be represented by the following

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reaction scheme. In the first scheme, tungsten(VI) hexachloride was reacted with oxalic acid dihydrate. These materials were reacted in the ratio: $WC1_6$: $3H_2C_2O_42H_2O$. This proportion was found to be the best after checking with different molar ratios of 1 : 1, 1 : 2, and 1 : 3.

The reaction conditions investigated were as follows: (1) Mechanical mixing of the two solid reactants was carried out. The reaction was completed after three days. (2) Tungsten hexachloride and oxalic acid were refluxed with toluene in a nitrogen atmosphere. (3) The oxalic acid was dissolved in distilled water. Solid tungsten hexachloride was added a little at a time to the oxalic acid solution. (4) The same procedure was adopted with methanol instead of water. (5) The procedure was repeated using concentrated hydrochloric acid instead of water.

Agitation and heating were necessary between 60 and 70°C for the last three cases. The color of the solutions in all the cases was green. The solutions were dried in vacuum.

Chemical analysis

Tungsten was determined in the compounds gravimetrically by the cinchonine procedure [5]. Oxalate was determined by titration with potassium permanganate [6]. The results of the analysis and theoretical values are presented in Table 1.

Thermal analysis

The decomposition of different oxalates was monitored by thermogravimetry (TG) and differential scanning calorimetry (DSC) on a DuPont 1090 thermal anlyzer. Experiments were run in a dynamic atmosphere of air and nitrogen, at a gas flow rate of 25 ml min^{-1}. 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}.

TABLE 1

Results of the analyses of the compounds

Routes	Compound	Found (%)		Theoretical (%)	
		W	$C_2O_4^{2-}$	W	$C_2O_4^{2-}$
Mechanical mixture	$WO_3(H_2C_2O_4)_32H_2O$	31.67	45.39	34.18	49.08
Distilled water	$WO_3(H_2C_2O_4)_36H_2O$	28.16	43.65	30.15	43.29
Methanol	$WO_2C_2O_4 \cdot 4H_2O$	45.10	22.17	48.92	23.41
Hydrochloric acid	$WO_2C_2O_4 \cdot H_2O$	61.78	26.19	57.12	25.89
Reflux	$WO_2C_2O_4 \cdot H_2O$	54.33	27.53	57.12	25.89

X-ray powder diffraction analysis

X-ray powder diffraction (XRD) was carried out on the product of the decomposition using a Philips X-ray diffractometer. Samples were analyzed by CuK_α radiation at 1.54 Å. The scannning rate was 1° 2θ min^{-1}.

Infrared analysis

These oxalates were examined using a diffuse reflectance infrared Fourier transform (DRIFT) technique in the range 4600–400 cm^{-1}. A KBr matrix was prepared containing this oxalate. The mass ratio of oxalate to KBr was 1 : 20.

RESULTS AND DISCUSSION

The results of the Fourier transform infrared spectra (FTIR) of the compounds (Table 2) show strong absorption due to the terminal νW = O band around 925 cm^{-1} [7]. The band due to hydroxyl of water of hydration occurs as a broad band around 3500 cm^{-1}.The bands between 1600–1700 cm^{-1} are attributed to ν_{as}(C = O), 1400–1560 cm^{-1} can be ascribed to the ν_s(C–O) + ν(C–C), around 1200 cm^{-1} to the ν_s(C–O) + δ(O–C = O), around 800 cm^{-1} to δ(O–C = O) + ν(M–O) and around 500 cm^{-1} to the ν(M–O) + ν(C–C). These bands are characteristic of the chelating oxalate group [8,9]. The band at approximately 700 cm^{-1} may be assigned to O–W–O grouping and a similar linkage has been reported in molybdenum oxalate

TABLE 2

FTIR data on tungsten oxalate

Band position (cm^{-1}) [a]	Probable assignment
3241 S,br	ν(OH)
1702 VS	ν_{as}C = O
1410 M	ν_s(C–O) + ν(C–C)
1260 S	ν_s(C–O) + δ(O–C = O)
923 M	νW = O
805 M	δ(O–C = O) + ν(M–O)
755 S	–O–W–O–
722 S	–O–W–O–
495 M	ν(M–O) + ν(C–C)
459 M	ν(M–O) + ν(C–C)
423 M	ν(M–O) + ring deformation
406 M	ν(M–O) + ring deformation

[a] (VS) Very strong; (S) strong; (M) medium; (br) broad; (s) symmetric; (as) asymmetric.

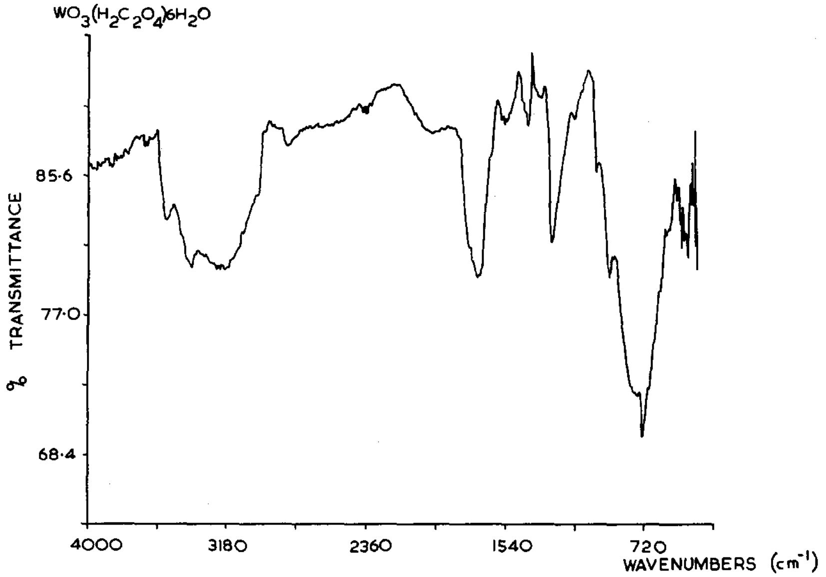

Fig. 1. FTIR spectra of tungsten oxalate when distilled water was the solvent.

preparation [10]. The ν(M–O) + ring deformation gives bands around 400 cm^{-1} [9] and such a band was also present in the preparations described here. Figure 1 shows the FTIR spectra of tungsten oxalate when distilled water was the solvent.

Thermal behavior of the compounds

The TG and DSC studies of the compounds was carried out in dry nitrogen and air. Tables 3 and 4 show that the oxalatotungstates lose their water in one stage which is observed in DSC as peaks approximately at 50°C. Figures 2 and 3 show the TG and DSC curves of tungsten-oxalate when distilled water was the solvent.

The decomposition from the anhydrous oxalate to the oxide takes place in one stage and it corresponds to the decomposition of either the oxalic acid adduct or the oxalate. In all cases, the anhydrous compound is stable below 100°C beyond which the decomposition starts. The decomposition attains a maximum around 150°C, the process is complete at around 250°C. In the DSC curve, the decomposition is observed as an endothermic peak in both nitrogen and air, centered around 150°C. This is in contrast to the molybdenum oxalate preparations which decomposed exothermically in both air and nitrogen.

The final product of decomposition shows a yellow colored tungsten oxide. This solid residue has been analyzed by X-ray powder diffraction which reveals the formation of WO_3. Table 5 gives a comparison of the

TABLE 3

WCl_6: $3H_2C_2O_4 \cdot 2H_2O$ TG data in atmosphere of N_2 and air

Routes	Decomposition medium	Dehydration		Decomposition		Residue	
		Temp. (°C)	(%)	Temp. (°C)	(%) (oxalate)	Temp. (°C)	(%)
Mechanical mixture	N_2	25–100	6.05	100–250	53.74	1000	39.94
	Air	25–105	5.04	105–237	49.88	1000	44.61
Distilled water	N_2	25–115	20.35	115–250	45.48	1000	35.51
	Air	25–108	28.87	108–250	47.34	1000	30.55
Methanol	N_2	25–100	34.43	100–250	8.69	1000	52.35
	Air	25–105	34.61	105–263	10.00	1000	54.67
Hydrochloric acid	N_2	25–100	1.97	100–300	20.40	1000	77.91
	Air	25– 95	2.25	95 –314	23.83	1000	73.81
Reflux	N_2	25–100	4.34	100–230	24.36	1000	68.52
	Air	25–101	4.89	101–249	23.30	1000	70.98

observed *d* values with the reported data for WO_3 [11]. This result is different from the result obtained from molybdenum oxalate [12] where molybdenum blue "blue oxide" is obtained which, as formed, is amorphous but then undergoes an exothermic recrystallization with some small mass change to give a crystalline oxide. The oxide described as molybdenum blue, due to its color, was, however, identified as MoO_3 from the X-ray diffraction pattern which is normally a white oxide. The reasons for this behavior in case of molybdenum were discussed in the previous paper. In the tungsten oxide, formed here from the decomposition of the tungstenoxalate precipitates, the yellow color of the oxide remained throughout from the temperature at which it was formed to the temperature at which it melted. However, the temperature did induce a gradual increase in crystallinity. The X-ray data reported in Table 5 was obtained only after heating at 700°C. Samples

TABLE 4

WCl_6: $3H_2C_2O_4 \cdot 2H_2O$ DSC data in atmosphere of N_2 and air

Routes	Peak temperature (°C)		Product color
	Dehydration	Decomposition	
Mechanical mixture	50	150	yellow
Distilled water	70	150	yellow
Methanol	50–70	– [a]	yellow
Hydrochloric acid	40	140	yellow
Reflux	50	130	yellow

[a] Peak does not have clearly defined maximum or minimum temperature.

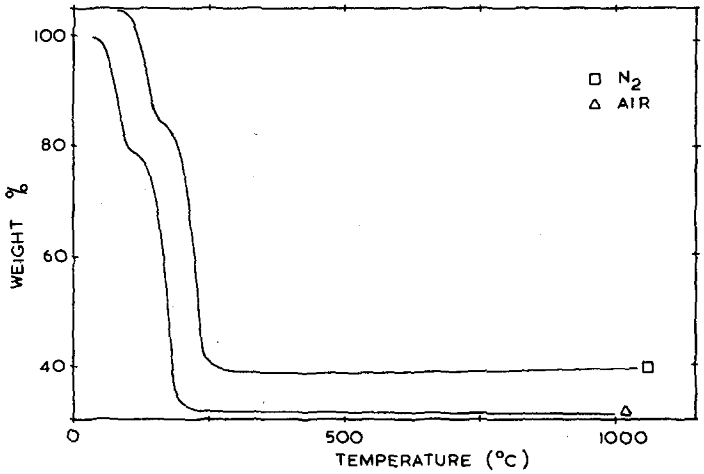

Fig. 2. TG curve of tungsten oxalate when distilled water was the solvent. Note: The TG curve in nitrogen has been displaced by 5% upwards and by 50°C.

heated below this temperature showed only the principle lines as indicated by the footnote to this table. It would appear that the amorphous structure observed in molybdenum oxide residues from oxalate decomposition, can only retain a certain degree of defect structure before reverting to a good

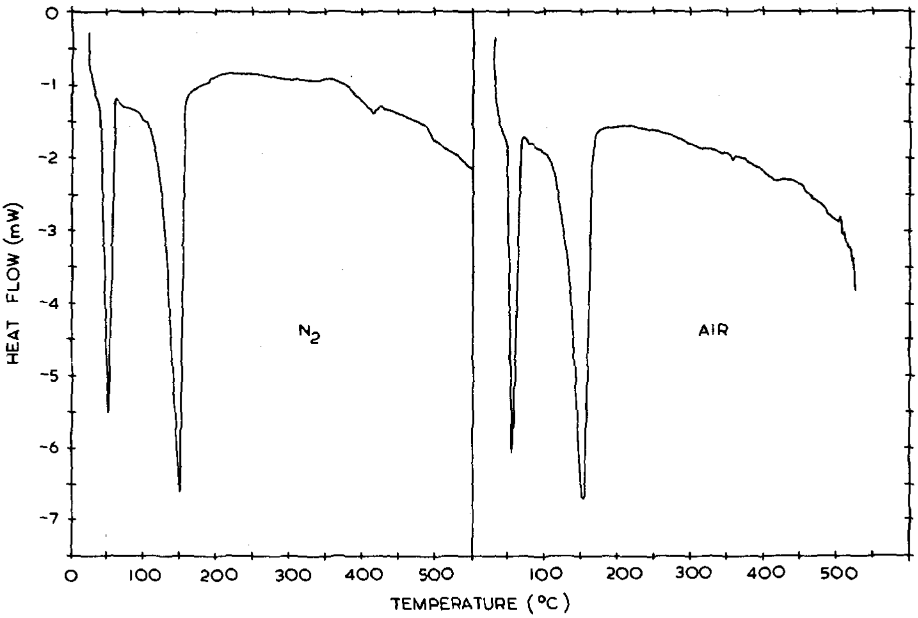

Fig. 3. DSC curve of tungsten oxalate when distilled water was the solvent.

TABLE 5

X-ray data of WO_3: $\lambda = 1.5418$ Å; "*d*" values (Å) for WO_3 at 700°C

"*d*" Values for sample prepared (Å)	I/I_0 [a]	"*d*" Values reported (Å)	I/I_0 [a]
3.88 [b]	S	3.90	40
3.69 [b]	VS	3.70	100
3.35	W	–	–
3.12	M	3.16	30
2.70 [b]	VS	2.70	85
2.64 [b]	S	2.63	40
2.18 [b]	S	2.18	45
2.02	W	2.01	30
1.93	M	1.95	20
1.89	M	1.86	50
1.83 [b]	S	1.84	40
1.71	M	1.73	35
1.68	M	1.68	50
1.65 [b]	S	1.66	60
1.55	W	1.57	20
1.54	M	1.53	60
1.49	M	1.50	40
1.39	W	1.37	8
1.34	W	1.35	20
1.31	W	1.32	20
1.24	M	1.26	50
1.22	W	1.24	20

[a] (VS) Very strong; (S) strong; (M) medium; (W) weak.

[b] Heating to 500°C gave only these lines.

crystalline material and the exothermic peak is a reflectence of this limit being reached. However, the same kind of change occurring in tungsten oxide occurs gradually over an extended temperature range, possibly due to the larger size of the tungsten ion enabling the oxygen ions to be more easily distributed around it.

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