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Note

SOME STUDIES ON THALLIUM OXALATES. III. THE THERMAL DECOMPOSITION OF THALLIUM(I) MONOHYDROOXALATE

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Lamy [1] prepared thallium(I) monohydrooxalate, $TlHC_2O_4$, by heating the thallium(I) monohydrooxalate hemihydrate, $TlHC_2O_4 \cdot \frac{1}{2} H_2O$. The preparation of thallium(I) monohydrooxalate hemihydrate is reported by Kuhlmann [2], Crookes [3] and Willm [4]. It is reported that water is given up at 30°C, forming anhydrous thallium(I) monohydrooxalate [5]. Thallium(I) monohydrooxalate is more soluble in water than thallium(I) oxalate, $Tl_2C_2O_4$ [6]. At 15.6°C, 5.338 g of anhydrous salt dissolves in 100 g of water [3], whereas at 100°C the salt dissolves in less than its own weight of water to form a syrupy solution [5], the solubility of thallous oxalate is only 1.577 g/100 g of water at 19.96°C. Thallium(I) monohydrooxalate crystals [5] belong to the monoclinic system and are either simple hexagonal flakes or prisms more flattened at the base.

So far, nobody appears to have reported on the thermal behaviour of thallium(I) monohydrooxalate. The present study deals with the authors' findings on the thermal behaviour, IR absorption, X-ray diffraction and microscopic studies of the salt.

EXPERIMENTAL

Instruments

The materials used and the methods employed are similar to those described previously [6,7]. A Stanton thermobalance was used for TG measurements, with a silica crucible as sample holder, and the heating rate was 4°C min^{-1}. For DTA, a fabricated unit with an automatic recorder was used, with platinum cups as sample holders, and recalcinated Al_2O_3 as the reference material. The heating rate was 4—5°C min^{-1}. A Perkin-Elmer 257 IR spectrophotometer (4000—625 cm^{-1}) and a Beckman IR-12 spectrophotometer (650—200 cm^{-1}) were used to obtain the IR spectra using the nujol mull technique in both regions. The X-ray powder photographs were taken by an X-ray diffractometer, with a Phillips X-ray generator PW1010 with copper K_α radiation. A Carl Zeiss polaroid microscope with an adoptable camera was used for microscopic observations and for taking the photomicrographs. A polarizing microscope with a universal stage was used to measure "2*V*" values.

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Preparation and chemical analysis

Thallium(I) monohydrooxalate was prepared [5] by mixing equimolar solutions of thallium(I) carbonate and oxalic acid in the ratio 1 : 2 by volume. The solution was slowly evaporated so as to reduce the volume and the compound was allowed to crystallize. The crystals were separated and washed with alcohol and dried under vacuum over silica gel, and its oxalate and thallium contents were determined [8]. The assay was found to correspond to the formula $TlHC_2O_4$; the results are given in Table 1.

Thermogravimetric analysis (TG)

The thermogram of thallium(I) monohydrooxalate was taken under atmospheric air. From the pyrolysis curve given in Fig. 1 it is obvious that the compound is thermally stable up to 200°C. From 200°C onwards it decomposes to thallium(I) oxalate up to 250°C and the loss in weight corresponds to 15.06% (the theoretical loss being 15.33%). Thallium(I) oxalate thus formed is stable up to 300°C, and there onwards it decomposes up to 380°C. This loss amounts to 14.4%, which corresponds to the decomposition of the thallium(I) oxalate to thallium(I) oxide (the theoretical loss being 14.5%). Thallium(I) oxide thus formed is stable up to 440°C and the gain amounts to about 2%. So, in the case of thallium(I) monohydrooxalate the thermal decomposition is via the formation of another oxalate, i.e. thallium(I) oxalate, which decomposes according to the mechanism reported earlier [6].

Differential thermogravimetric analysis (DTG)

The DTG curve of thallium(I) monohydrooxalate is given in Fig. 2. The first sharp peak with ΔT_{max} at 240°C corresponds to the decomposition of thallium(I) monohydrooxalate to thallium(I) oxalate. The second peak with ΔT_{max} at 340°C corresponds to the decomposition of thallium(I) oxalate to thallium(I) oxide. The third peak with ΔT_{min} at 420°C corresponds to the partial oxidation of thallium(I) to thallium(III), thus forming a mixture of thallium(I) and thallium(III) oxides.

TABLE 1

Chemical analysis data of thallium(I) monohydrooxalate

Wt. of sample (mg)	Wt. of oxalate ion (mg)	Wt. of thallium(I) (mg)	% oxalate	% Thallium(I)	Ratio of Tl^+ to $C_2O_4^{2-}$
99.0	29.40	68.30	29.70	69.00	1.0000
205.2	61.05	141.70	29.75	69.06	0.9993

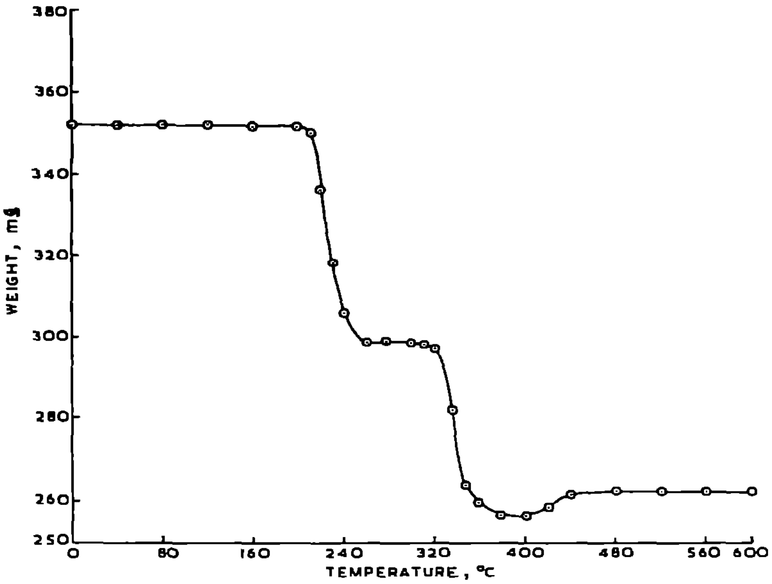

Fig. 1. Pyrolysis curve of thallium(I) monohydrooxalate.

Differential thermal analysis (DTA)

The DTA of thallium(I) monohydrooxalate was carried out under atmospheric pressure and the curve is given in Fig. 3. The endothermic peak with ΔT_{min} at 205°C corresponds to the decomposition of thallium(I) monohydrooxalate to thallium(I) oxalate. The exothermic peak with a doublet of maxima around 355°C corresponds to the decomposition of thallium(I) oxalate to thallium(I) oxide. A sharp exothermic peak with ΔT_{max} at 422°C

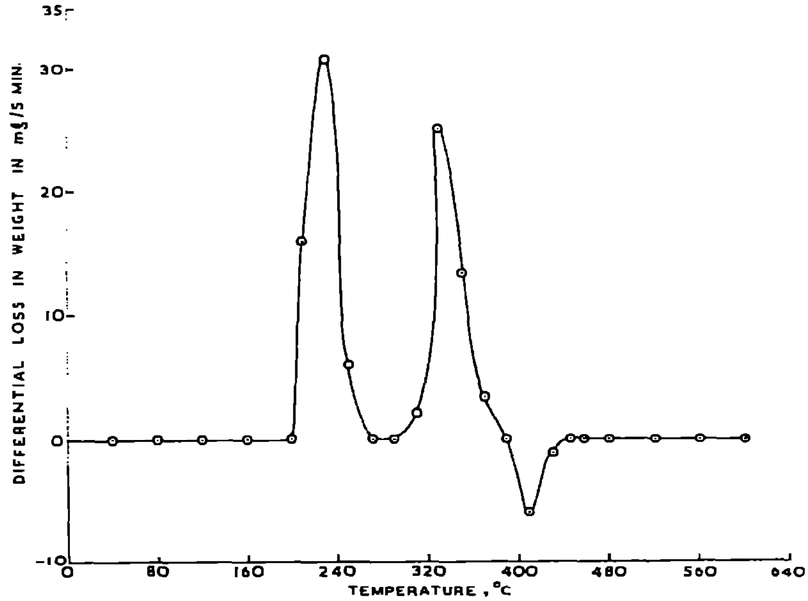

Fig. 2. DTG curve of thallium(I) monohydrooxalate.

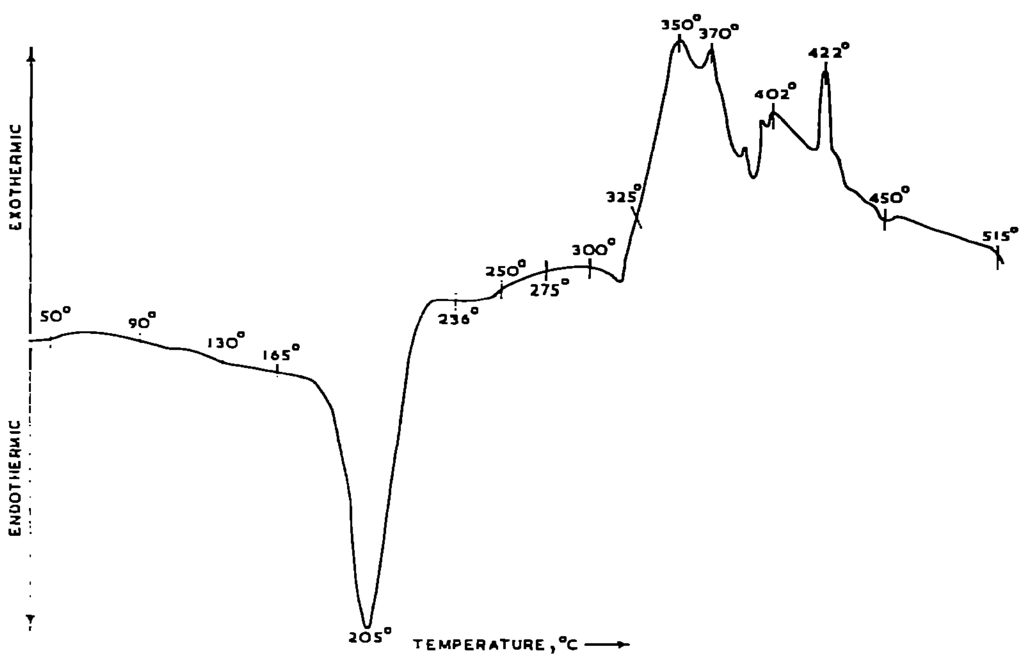

Fig. 3. DTA curve of thallium(I) monohydrooxalate.

corresponds to the gradual and partial oxidation of thallium(I) to thallium(III). These thermal changes finally lead to the formation of a mixture of thallium(I) and thallium(III) oxides.

From these observations the thermal decomposition mechanism of thallium(I) monohydrooxalate may be given as

$$2\ \mathrm{TlHC_2O_4} \xrightarrow{200-250^\circ\mathrm{C}} \mathrm{Tl_2C_2O_4} + \mathrm{H_2O} + \mathrm{CO} + \mathrm{CO_2}$$

$$\mathrm{Tl_2C_2O_4} \xrightarrow{300-380^\circ\mathrm{C}} \mathrm{Tl_2O} + \mathrm{CO} + \mathrm{CO_2}$$

$$\mathrm{Tl_2O} \xrightarrow[(\mathrm{O_2})]{400-440^\circ\mathrm{C}} x\mathrm{Tl_2O_3} + y\mathrm{Tl_2O}$$

Microscopic observations

The photomicrographs of thallium(I) monohydrooxalate and its heated product obtained at 250°C are given in Fig. 4a and b. In both cases the crystals were developed on the microscopic slides from the respective saturated solutions of the compounds in water.

From Fig. 4a it is clear that the crystals of thallium(I) monohydrooxalate are hexagonal flakes, and are highly birefringent, biaxial with symmetrical extinction. The crystals in Fig. 4b are colourless flakes with nearly square surfaces, transparent and highly birefringent with symmetrical extinction. These crystals are biaxial and negative with a $2V$ value of 70° and are indentical to those of thallium(I) oxalate [6]. From these observations it is clear that the first decomposition product of thallium(I) monohydrooxalate is thallium(I) oxalate.

Fig. 4. (a) Thallium(I) monohydrooxalate. (b) Heated (250°C) product of thallium(I) monohydrooxalate.

X-Ray diffraction data

Prominent peaks of the X-ray diffraction data of thallium(I) monohydrooxalate and the intermediate are given in Table 2. The "*d*" values corresponding to the prominent peaks of the diffraction patterns of the intermediate of thermal decomposition and thallous oxalate [6] coincide, confirming them to be one and the same; so the first decomposition product of thallium(I) monohydrooxalate must be thallium(I) oxalate. These observations are in agreement with the proposed mechanism of thermal decomposition.

TABLE 2

X-Ray diffraction data, d(Å)

$TlHC_2O_4$	Intermediate
10.222_3	6.534_1
5.421_2	4.343_2
4.462_x	3.802_3
4.013_6	3.453_x
3.433_5	3.261_5
3.192_6	2.903_2
3.126_5	2.767_5
3.043_2	2.667_2
2.840_2	2.189_4
2.801_2	2.038_2
2.718_7	1.866_2
2.338_2	
2.293_2	
2.233_5	
2.176_2	
2.090_2	
2.062_2	
1.831_2	
1.731_1	

TABLE 3

Comparison of IR spectral data of thallium(I) monohydrooxalate, intermediate product of its thermal decomposition and thallium(I) oxalate (cm^{-1})

Thallium(I) monohydrooxalate		Thallium(I) oxalate	Assignment
Original	Heated at 250°C		
1760 Sp, VSt			Unionized COOH
1595 B, VSt	1600 B	1625 M	
	1570 B	1575 M	ν(C=O)
1530 Sh, VW	1530 B, St	1530 Sp, M	
1315 Sh	1310 Sh	1325 VW	
		1310 M	ν(C=O) + δ(O—C=O)
1290 Sp	1295 Sp, VSt	1275 Sp, St	
1250 Sp, St			
765 Sp, VSt	755 Sp, VSt	753 VSp, St	
		748 VSp, St	δ(O—C=O) + ν(M—O)
	730 VSp, St	730 VSp, St	
	390 Sh	390 Sh	δ(O—C=O) + ν(C—C)
	355 Sp, M	355 Sp, M	
	320 B, W	320 B, W	
	300 W	300 Sh, W	
	225 B, M	225 B, M	δ(O—C=O)

VW, very weak; W, weak; M, medium; B, broad; St, strong; Sp, sharp; Sh, shoulder.

IR spectral studies

The IR spectral data of thallium(I) monohydrooxalate and the product obtained by heating the compound at 250°C are given in Table 3. A sharp, very strong peak at 1760 cm^{-1} indicates the presence of unionized COOH [9] in thallium(I) monohydrooxalate. A sharp, very strong peak at 1595 and a shoulder at 1530 cm^{-1} indicate the presence of stretching modes of vibration of C=O. A shoulder at 1315 and a sharp peak at 1290 cm^{-1} indicate the presence of bending modes of vibration of O—C=O, while a sharp, very strong peak at 765 cm^{-1} indicates the presence of M—O bonding in thallium(I) monohydrooxalate.

The similarity in the spectral data of the heated product and thallium(I) oxalate confirms that the product obtained by heating $TlHC_2O_4$ at 250°C is nothing but $Tl_2C_2O_4$. These observations are also in agreement with the proposed mechanism of thermal decomposition.

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