

ISOLATION OF THALLIUM (I) DIAQUODIOXALATODIOXOURANIUM (VI) AND ITS THERMAL BEHAVIOUR

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$Tl_2 [UO_2(C_2O_4)_2(OH_2)_2]$ was prepared and characterised by chemical analysis, X-ray diffraction and IR spectroscopy. On thermolysis in air, the compound gave at $300^\circ C$, Tl_2UO_4 , which on prolonged keeping in air in the range of 300° – $500^\circ C$, was converted into a mixture of thallic oxide and thallium (I) diuranate. Again at $580^\circ C$, the thallic oxide and thallium diuranate mixture was transformed back into Tl_2UO_4 . Vacuum decomposition studies of the oxalate were also made.

INTRODUCTION

Thallium (I) resembles, in many respects, the argentous ion and the ions of the heavier alkali metals in its crystallochemical behaviour due to the similarity in size. Thus, $Tl[UO_2(OOCCH_3)_3]$ has been shown to be isostructural with potassium, rubidium, ammonium and silver double acetates of uranium (VI) (Ferrari *et al.* 1959). As an extension of our studies on thallium uranium carboxylates (Aravamudan and Sampath 1970), conditions favouring the formation of anionic oxalate complexes of uranium (VI) featuring thallium as cation were studied. In this paper is presented our work on the isolation, characterisation and thermal behaviour of thallium (I) diaquodioxalatodioxouranium (VI) in air and at low pressures (10^{-2} mm/Hg.) On thermal decomposition $Tl_2[UO_2(C_2O_4)_2(OH_2)]$ gives Tl_2UO_4 in ambient conditions. At low pressures, in addition to Tl_2UO_4 a lower-valent thallium uranium oxide is formed. Tl_2UO_4 in air is thermodynamically unstable with respect to Tl_2O_3 and $Tl_2U_2O_7$, and undergoes slow oxidation between 300 – 400° to give a mixture of Tl_2O_3 and $Tl_2U_2O_7$. This mixture in air above 550° gives back Tl_2UO_4 .

EXPERIMENTAL DETAILS

About 1.25 g (3 millimoles) Uranyloxalate trihydrate and 1.5 g (3 millimoles) of anhydrous thallic oxalate were dissolved in 50 ml. of 5 per cent oxalic acid and the solution was evaporated in dark on a water bath till yellow crystals separated out. The crystals were filtered, washed with acetone and air-dried. Thallium was determined as thallic chromate after removing uranium as uranyl peroxide. Uranium was determined as U_3O_8 and the oxalate was determined permanganometrically.

X-ray powder patterns were taken using Cu-K α radiation and a 114.6 mm diameter camera. The infra-red measurements were made using KBr pellet technique in a Carl-Zeiss model UR-10 spectrophotometer in the range 400–4000 cm⁻¹. The thermogravimetric studies in air were carried out in platinum crucibles using a Stanton (HT-SM model) recording thermobalance. The differential thermal analysis experiments in air were done using a self-constructed recording DTA unit employing chrome-alumel thermocouples and ignited alumina as the reference material. Thermal studies at low pressures were made heating the system under continuous evacuation at 10⁻² mm/Hg.

RESULTS AND DISCUSSION

The infra-red data of thallium (I) diaquodioxalatodioxouranium (VI) are presented in Table I.

TABLE I
Infra-red data on [Tl₂UO₂(C₂O₄)₂(OH₂)₂]

Band frequency cm ⁻¹	Assignment
1670–1600 (b,s)	$\nu_{asy}(C=O) + \delta(H-O-H)$
1430 (m)	$\nu_{sym}(C=O)$
1380 (s)	$\nu_{sym}(C-O) + \delta(O-C=O)$
1270 (sh)	
910 (s)	$\nu(C-C) + \nu_{asy}(UO_2)$
825 (w)	$\nu_{sym}(UO_2)$
770 (s)	$\delta(O-C-O)$
480 (w,b)	$\delta_{sym}(O-C-O)$

b=broad s=strong m=medium w=weak sh=shoulder

The presence of uranyl group is indicated by the bands at 910 cm⁻¹ and at 825 cm⁻¹. The bending mode of water around 1610 cm⁻¹ coincides with the symmetric stretching mode of C=O of the oxalate making it difficult to say whether the compound is hydrated oxo- complex or hydroxy- complex. However, thermal analysis showed water loss at moderate temperatures, thereby indicating that the compound is to be considered as an oxo- complex rather than hydroxy- complex. Also an hydroxo complex would necessitate the absence of UO₂ frequencies which were, however, actually shown to be present as discussed above.

The thermal decomposition of [Tl₂[UO₂(C₂O₄)₂(OH₂)₂] was investigated both at ambient and reduced pressures to find out the nature of the ultimate solid phase formed. In the absence of air there is possibility of lower valent uranium compounds being realised, such as observed in decomposition of uranyl oxalate trihydrate.

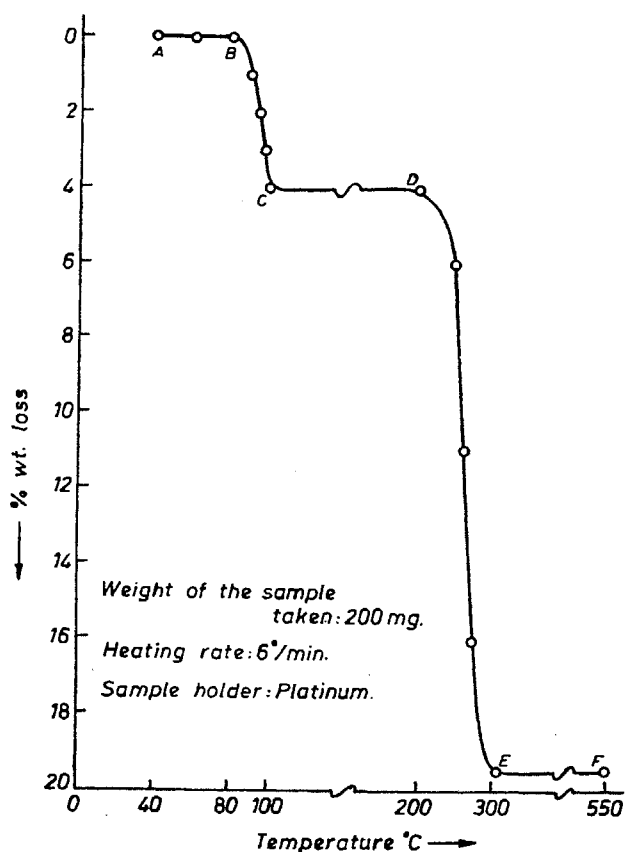
Thermogravimetric data in air of thallium (I) diaquodioxalatodioxouranium (VI) is plotted in Fig. 1. In Table II are given the 'd' spacings of [Tl₂(UO₂(C₂O₄)₂(OH₂)₂)] and the various solid phases obtained during its thermal decomposition.

TABLE II

'd' Spacings in Å of Thallium-Uranium compounds

$Tl_2[UO_2(C_2O_4)_2(OH)_2]$	4.55 (m), 4.32 (m), 3.84 (w), 3.56 (w), 3.31 (s), 3.18 (m), 3.05 (m), 2.32 (m), 2.19 (m), 2.12 (s), 2.04 (v.w.), 1.95 (w), 1.91 (s), 1.85 (w), 1.81 (w), 1.73 (v.w.).
$Tl_2U_2O_7$	3.42 (v.s.), 3.19 (s), 3.01 (w), 2.82 (m), 2.05 (s), 1.96 (s), 1.76 (s), 1.72 (s) 1.70 (s).
Tl_2UO_4	3.16 (v.s.), 2.89 (v.s.), 2.68 (v.w.), 2.54 ((m), 2.05 (m), 1.91 (s), 1.72 (w), 1.60 (m), 1.57 (s), 1.45 (w).
Tl_2O_3	4.14 (w), 2.99 (v.s.), 2.60 (s), 2.44 (w), 2.21 (w), 2.03 (m), 1.84 (s), 1.69 (w), 1.61 (v.w.), 1.58 (s), 1.54 (w), 1.50 (m), 1.33 (v.w.), 1.31 (w), 1.29 (w), 1.21 (v.s.), 1.20 (s).

S=strong, w=weak m=medium, v.s.=very strong, v.w.=very weak

Fig. 1. TGA curve of $Tl_2[UO_2(C_2O_4)_2(OH)_2]$ in air

$Tl_2 [UO_2(C_2O_4)_2 (OH_2)_2]$ started losing water at $60^\circ C$ and the loss of water was complete at $100^\circ C$ (portion BC in the figure) and between 100 to 260° the anhydrous compound was stable (CD, Fig. 1) and between 280° and 300° there was rapid weight-loss (DE, Fig. 1). After $300^\circ C$ there was no weight change upto 550° EF, Fig. 1). The product at 300° was mostly orange in colour with some black carbon particles and the X-ray pattern corresponded to Tl_2UO_4 . It was observed that, Tl_2UO_4 on heating in air between 300 – $400^\circ C$ for a long time gave a mixture of thallic oxide (black) and $Tl_2U_2O_7$ (orange). The solid phases were identified by characteristic X-ray patterns. The amount of thallic oxide formed during this slow oxidation of Tl_2UO_4 according as



was determined by extracting the mixture ($Tl_2UO_4 + Tl_2U_2O_7 + Tl_2O_3$) with 2N hydrochloric acid and estimating the Tl(III) iodometrically. The $Tl_2O_3 + Tl_2U_2O_7$ mixture on heating in air to higher temperature (550 – 580°) for a prolonged period gave back Tl_2UO_4 with a concomitant loss of oxygen. The phase $Tl_2U_2O_7$, unlike Tl_2UO_4 was resistant to oxidation even upto $600^\circ C$. This is the first time that such an observation has been made in Tl-U-O system.

Thermal studies carried out at low pressure at 300° on $Tl_2[UO_2(C_2O_4)_2] \cdot (OH_2)_2$ gave Tl_2UO_4 and a lower valent thallium uranium oxide. The characterisation of the lower valent thallium uranium oxide is in progress.

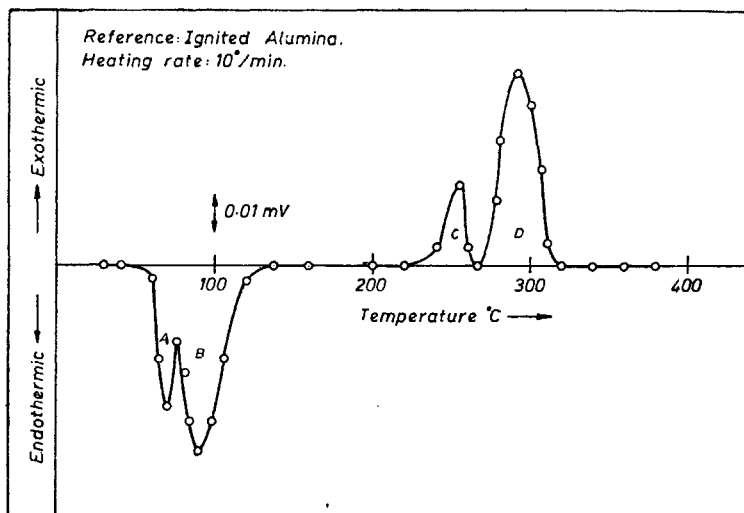


Fig. 2. DTA of $Tl_2 [UO_2 (C_2O_4)_2 (OH_2)_2]$ in air

The differential thermal analysis curve (Fig. 2) of $Tl_2 (UO_2 (C_2O_4)_2 (OH_2)_2)$ in air showed two endothermic peaks (A and B) at about 90° and two close exothermic peaks initiating at 240° and peaking at about 290° (C and D). The endothermic peaks are due to water-loss in steps. The exothermic peaks are associated with enthalpy changes accompanying the decomposition of $Tl_2 (UO_2 (C_2O_4)_2 (OH_2)_2)$ to Tl_2UO_4 .

Due to the rapidity of the intermediate processes occurring during the reaction it was difficult to assign enthalpy changes to single individual steps.

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