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SOME STUDIES ON THALLIUM OXALATES. VI

THALLIUM(I) BIS-OXALATO DIAQUO THALLATE(III) TRIHYDRATE

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The effect of the thallium(I) concentration on the potentiometric titration of thallium(III) with oxalic acid in 0.1 *M* HNO_3 or 0.05 *M* H_2SO_4 is studied, and conditions are established for the preparation of the thallium(I) bis-oxalato diaquo thallate(III) complex. Chemical analysis of the salt corresponds to the formula $Tl^I(Tl^{III}(C_2O_4)_2) \cdot 5\,H_2O$. Thermal decomposition studies on the complex using TG, DTG and DTA techniques indicate the formation of thallium(I) oxalate (stable from 130° to 320°) as the intermediate, the final product being a mixture of thallium(I) oxide and thallium(III) oxide (stable from 520° to 600°). Infrared absorption spectra, X-ray diffraction patterns and microscopic observations are used to characterise the complex and the intermediate.

Suitable conditions for the formation of the bis-oxalato diaquo thallate(III) complex in which the metal-ligand ratio is 1 : 1.5 have been reported [1]. The presence of a sufficient concentration of NH_4^+, K^+, Rb^+, Cs^+, Sr^{++} or Ba^{++} in the potentiometric titration of thallium(III) with oxalic acid was found to alter the metal-ligand ratio from 1 : 1.5 to 1 : 2 [1, 2]. The present article deals with the effect of variation of the thallium(I) ion concentration on the formation of and some studies on the bis-oxalato thallate(III) complex.

Experimental

The materials used and the methods employed were similar to those already described [3, 4]. The DTA apparatus used was fabricated according to standardised designs. The heating rate was 4–5°/min. Platinum cups were used as sample holders, and recalcined Al_2O_3 as the reference material.

Effect of the thallium(I) concentration on the potentiometric titration of thallium(III) with oxalic acid

Thallium(III) (0.1 mmole) was titrated potentiometrically with oxalic acid (0.1 *M*) in the presence of various concentrations of thallium(I) under the conditions already reported [1] (0.125 *M* HNO_3), and the results are given in Fig. 1. From the Figure it is evident that the number of moles of oxalic acid required per mole of thallium(III) increases from 1.5 to 2.0 with the increase in the concentration of thallium(I) nitrate. It is also evident that there is a larger break in the inflection point in the presence of thallium(I), and the mole ratio of oxalic acid corresponding to the maximum break in potential is dependent upon the concentra tion of thallium(I) nitrate up to 0.005 *M*.

Similar experiments in 0.0625 *M* sulphuric acid media also show that the metal-ligand ratio is 1 : 2 in 0.0025 *M* or more Tl_2SO_4. In both the acid media the ratio

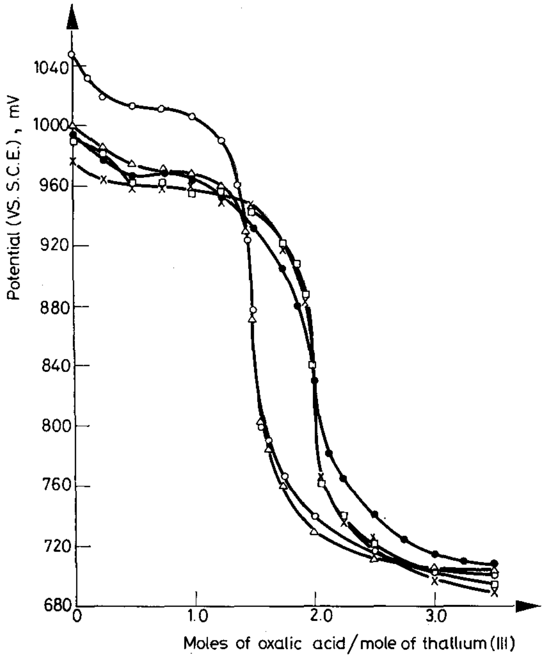

Fig. 1. Effect of variation of thallium(I) nitrate concentration on the potentiometric titration curve of thallium(III) nitrate with oxalic acid in 0.125 *M* nitric acid medium

(Tl^{III} : Ox^{2-}) remains the same (1:2) even up to 0.05 *M* Tl(I). Thus, the complex is prepared under the conditions where

$$[Tl^+] = 0.01\ M, \text{ and } [HNO_3] = 0.1\ M \text{ or } [H_2SO_4] = 0.05\ M.$$

Preparation of the complex

About 40 ml 0.1 *M* thallium(III) nitrate (or sulphate) in 1 *M* nitric acid (or 0.5 *M* sulphuric acid) was taken in a 600 ml beaker, to which 40 ml 0.1 *M* thallium(I) nitrate (or sulphate) and 280 ml distilled water was added slowly while the contents were stirred to avoid the precipitation of thallium(III) hydroxide due to a local rise in pH. Then, about 40 ml 0.2 *M* oxalic acid was added very slowly (dropwise from a burette), while the contents were stirred vigorously. The complex salt was allowed to settle, filtered and washed several times with 0.1 *M* nitric (or 0.05 *M* sulphuric) acid to free it from the excess of oxalic acid. Finally, the precipitate was dried in a vacuum desiccator over silica gel.

Chemical analysis

The oxalate and thallium contents of the compound were determined according to the methods developed by Sagi et al. [5, 6]. The water content of the complex was determined by difference and was in conformity with the thermogravimetric data.

$$\mathrm{Tl(I)} = 30.30\%; \qquad \mathrm{Tl(III)} = 30.27\%$$
$$C_2O_4^{2-} = 26.04\%; \qquad H_2O = 13.50\%$$

The above data correspond to the formula $\mathrm{Tl^ITl^{III}(C_2O_4)_2 \cdot 5\,H_2O}$. As thallium(III) is known to exhibit octahedral coordination [7], the structural formula of the compound may be given as $\mathrm{Tl^I[Tl^{III}(C_2O_4)_2(H_2O)_2] \cdot 3\,H_2O}$, which is confirmed by the following studies.

Thermal studies

The TG, DTG and DTA curves of thallium(I) bis-oxalato diaquo thallate(III) trihydrate are given in Fig. 2. From the pyrolysis curve it is clear that the continuous loss from 80° to 130° corresponds to the complete dehydration and redox decomposition of the thallium(III) oxalate to thallium(I) oxalate, and this is also indicated by a sharp DTG peak with $\Delta T_{\max}$ at 130°. The loss in weight corresponds to 26.90% (the theoretical loss being 26.40%). The thallium(I) oxalate thus formed is thermally stable from 130° to 320°, but decomposes from 320° to 400°, forming thallium(I) oxide with a weight loss of 14.5%. The loss in weight is maximum around 360°, which is indicated by the second DTG peak with $\Delta T_{\max}$ at 360°. From 400° to 520° a part of the thallium(I) oxide is oxidised to thallium(III) oxide, with an increase in weight corresponding to about 2%, and is indicated by the third peak in the DTG with $\Delta T_{\min}$ at 440°.

In the DTA curve the stepwise dehydration of the complex is indicated by a small endothermic peak around 80° and a sharp endothermic peak at 120°. The redox decomposition immediately following the dehydration of the complex is indicated by an exothermic peak with maximum at 130°. The sequence of these peaks in the DTA curve confirms that the dehydration precedes the redox decomposition of the complex. An exothermic peak at 350° corresponds to the decomposition of thallium(I) oxalate to thallium(I) oxide, and another at 420° to the oxidation of a part of the thallium(I) oxide to thallium(III) oxide.

The decomposition mechanism of the complex on the basis of these observations may be given as:

$$\mathrm{Tl^ITl^{III}(C_2O_4)_2 \cdot 5\,H_2O \rightarrow Tl^ITl^{III}(C_2O_4)_2 \cdot 2\,H_2O} \tag{1}$$

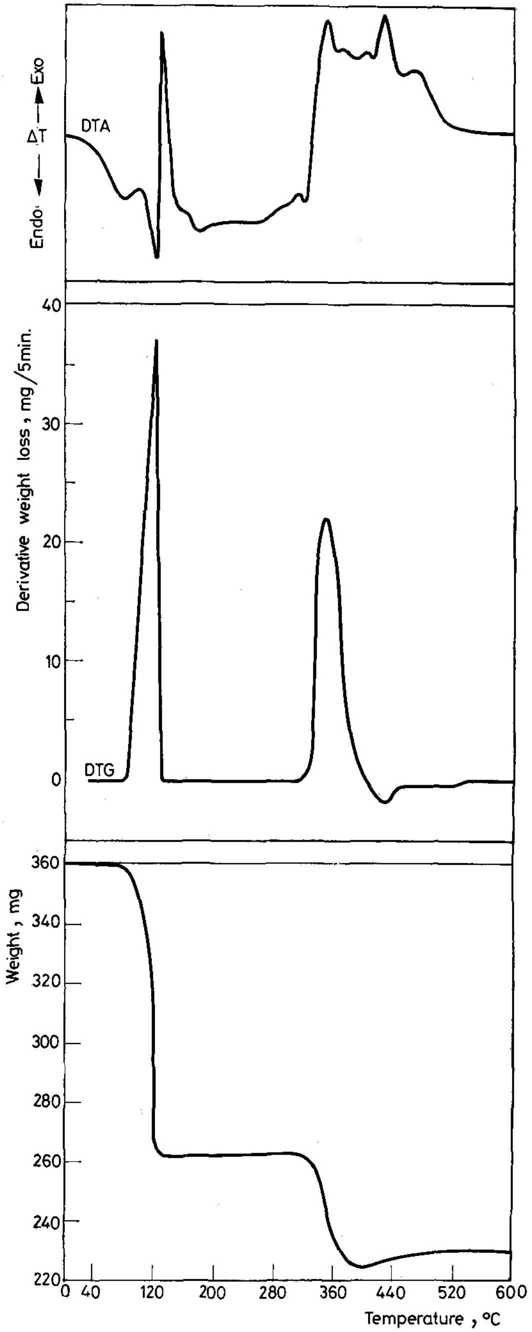

Fig. 2. TG, DTG and DTA curves of thallium(I) bis-oxalato diaquo thallate(III) trihydrate

$$\mathrm{Tl^{I}Tl^{III}(C_2O_4)_2 \cdot 2\,H_2O \rightarrow Tl^{I}Tl^{III}(C_2O_4)_2} \tag{2}$$

$$\mathrm{Tl^{I}Tl^{III}(C_2O_4)_2 \rightarrow Tl_2C_2O_4} \tag{3}$$

$$\mathrm{Tl_2C_2O_4 \rightarrow Tl_2O} \tag{4}$$

$$\mathrm{Tl_2O \rightarrow \mathit{x}Tl_2O + \mathit{y}Tl_2O_3}$$

Isothermal decomposition studies carried out at different temperatures show that the intermediate (1) can be isolated by heating the complex isothermally at 70°. Separate experiments on the electrical conductivity of the hydrated complex also gave information supporting this view.

Similar attempts to remove the coordinated water from the intermediate (1) to get the intermediate (2), by heating the complex isothermally at different temperatures, were unsuccessful. In all these experiments the redox decomposition of the complex immediately follows the dehydration. Hence, it appears that the stability of the complex is dependent upon the presence of coordinated water in the complex. Accordingly, the isolation of thallium(I) bis-oxalato thallate(III) without the coordinated water (intermediate (2)) is not possible.

Infrared spectral studies

The infrared spectral data on thallium(I) bis-oxalato diaquo thallate(III) trihydrate and the product obtained by heating the complex at 150° are given in Table 1. Very strong and broad absorption peaks at 3480 [8] and 1600 cm^{-1} [9] confirm the presence of water in the complex. A very sharp and very strong absorption for the complex at 805 cm^{-1} [10] confirms the presence of water in the coordinated form. A medium peak at 610 cm^{-1} [10] indicates the presence of lattice water in the complex.

The absence of such absorption peaks in the spectrum of the heated product of the complex shows the absence of water in the heated product.

From the data in Table 1 it is also clear that the product obtained by heating the complex to 150° is simply thallium(I) oxalate. The stretching frequencies of the metal-oxygen bond in thallium(I) oxalate are at 770 and 750 cm^{-1}, whereas in the complex the corresponding frequencies are shifted to 805 and 725 cm^{-1}, suggesting an increase in covalency between the thallium(III) and the oxygen of the oxalate in the complex. The difference in the natures of the bonding between the metal and the oxalate in thallium(I) oxalate and in the complex is also evident from the difference in the absorption peaks at 510 and 260 cm^{-1} in the complex, and at 530, 355 and 225 cm^{-1} in thallium(I) oxalate.

X-ray diffraction data

The X-ray diffraction data on thallium(I) bis-oxalato diaquo thallate(III) trihydrate, the intermediate obtained at 150° and thallium(I) oxalate are given in

Table 1

Comparison of infrared spectral data on the complex (thallium(I) bis-oxalato diaquo thallate(III) trihydrate), the complex heated at 150° and thallium(I) oxalate (cm^{-1})

Complex		Thallium(I) oxalate	Assignment
Original	Heated at 150°		
3600 –			ν as & s(H–O–H)
3400 VB, VSt			
1650 –			ν(C=O) + δ(H–O–H)
1550 VB, VSt			
	1625 M	1625 M	ν(C=O)
	1570 B	1575 M	
	1525 B, St	1530 Sp, M	
1320 Sh	1325 Sh	1325 VW	ν(C=O) + δ(O–C=O)
	1310 Sh	1310 M	
	1275 Sp, VSt	1275 Sp, St	
805 VSp, VSt			Coordinated water & δ(O–C=O) + ν(M–O)
	770 Sh	770 Sh, W	δ(O–C=O) + ν(M–O)
	753 VSt	753 VSp, St	
		748 VSp, St	
725 M			
610 M			Lattice water
510 VSt, B	530 VSt, B	530 VSp, VSt	ν(M–O) + δ(O–C=O)
		390 Sh	δ(O–C=O) + ν(C–C)
	350 Sp, VSt	355 Sp, M	
		320 B, W	
	310 Sh		
		300 Sh, W	
280 –	220 Sh	225 B, M	δ(O–C=O)
240 B			

Legend: *V* – Very; W – Weak; M – Medium; B – Broad; St – Strong; Sp – Sharp; Sh – Shoulder.

Table 2. From the data in Table 2 it is clear that the "*d*" spacings and the corresponding intensities for the heated product and thallium(I) oxalate coincide, confirming that the intermediate at 150° is thallium(I) oxalate. The X-ray diffraction data on the complex are useful in differentiating the complex from the other bis-oxalato thallate(III) complexes [3, 4, 11].

Microscopic observations

The crystals obtained from the aqueous solution of the compound obtained by heating the complex at 150° are colourless, transparent and base-flattened flakes. They are highly birefringent with symmetrical extinction, biaxially negative with a "2*V*" value of 70°, and are exactly similar to those of thallium(I) oxalate [3]. This confirms that the intermediate obtained at 150° is thallium(I) oxalate.

Table 2

X-ray diffraction data, *d*, (Å)

Complex	Intermediate	Thallium(I) oxalate
7.053_2	6.511_3	6.511_2
6.511_1	4.311_2	4.311_2
4.835_3	3.802_4	3.802_3
4.343_3	3.447_x	3.440_x
3.513_4	3.261_5	3.278_6
3.353_x	3.116_4	3.110_4
3.273_4	2.759_5	2.763_7
2.917_4	2.666_2	2.660_3
2.759_5	2.516_1	2.522_2
2.667_4	2.189_4	2.186_6
2.532_2	2.042_2	2.010_2
2.330_2	1.863_2	1.863_4
2.177_4	1.748_1	1.752_3
2.137_3		
2.038_2		
1.975_2		
1.882_3		

All these observations are in agreement with the proposed structure and the mechanism suggested for the thermal decomposition of the complex.

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RÉSUMÉ — On étudie l'effet de la concentration en thallium(I) sur le dosage potentiométrique du thallium(III) par l'acide oxalique 0.1 *M* HNO_3 ou 0.05 *M* H_2SO_4 et on établit les conditions de préparation du complexe de thallium(I)-bisoxalato-diaquothallate(III). L'analyse chimique du sel obtenu correspond à la formule $Tl^{I}(Tl^{III}(C_2O_4)_2) \cdot 5\ H_2O$. L'étude par TG, DTG et DTA de la décomposition thermique du complexe indique la formation d'oxalate de thallium(I) (stable de 130° à 320°) en tant qu'intermédiaire et d'un mélange de oxydes de thallium(I) et de thallium(III) (stable de 520° à 600°) comme produit final. Le complexe et l'oxalate thalleux intermédiairement formé, ont été caractérisés par absorption infrarouge, diffraction des rayons X, observations microscopiques et mesures de la conductivité électrique.

ZUSAMMENFASSUNG — Der Einfluß der Konzentration von Thallium(I) auf die potentiometrische Titration von Thallium(III) mit oxalsäure in 0.1 *M* HNO_3 oder 0.05 *M* H_2SO_4 wird untersucht und die Bedingungen für die Synthese von Thallium(I)bisoxalato-Diaquothallat-(III) werden ermittelt. Die chemische Analyse des erhaltenen Salzes entspricht der Formel $Tl^{I}(Tl^{III}(C_2O_4)_2) \cdot 5\ H_2O$. Die Untersuchungen der thermischen Zersetzung des Komplexes durch TG, DTG und DTA weisen darauf hin, daß sich Thallium(I)oxalat (stabil von 130° bis 320°) als Zwischenprodukt und als Endprodukt eine Mischung von Thallium(I)oxid und Thallium(III) oxid (stabil von 520° bis 600°) bilden. Infrarot-Absorptionsspektren, Röntgendiffraktionsuntersuchungen, mikroskopische Beobachtungen und Messungen der elektrischen Leitfähigkeit werden zur Charakterisierung des Komplexes und des gebildeten Thallooxalat Zwischenproduktes herangezogen.

Резюме — Изучено влияние концентрация таллия(I) на потенциометрическое титрование таллия(III) щавелевой кислотой в растворе 0.1 *M* HNO_3 или 0.05 *M* H_2SO_4. Установлены условия получения таллий(I)-бис-оксалато-диакво-таллата(III) комплекса. Химический анализ полученной соли соответствует формуле $Tl^{I}[Tl^{III}(C_2O_4)_2] . 5H_2O$. Проведенное термическое разложение комплекса с помощью ТГ, ДТГ и ДТА, показало образование в качестве промежуточного продукта оксалата таллия(I), стабильного от 130 до 320°. Конечный продукт разложения представлял собой смесь окисей таллия(I) и таллия(III), стабильных между 520 и 600°. ИК спектры, рентгенография, микроскопические наблюдения и измерения электрической проводимости были использованы для характеристики комплекса и образующегося оксалата таллия(I), как промежуточного продукта.