

NOVEL THERMAL DECARBOXYLATION OF TRIS(MANDELATO)–THALLIUM(III) COMPLEX

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ABSTRACT

Thermogravimetric studies (TG, DTG and DTA) of $Tl(MAN)_3$, where MAN stands for the anion of mandelic acid, indicated successive decarboxylation of the mandelate moieties. The kinetic parameters for the overall decarboxylation were determined employing several computational methods. The structure of the complex was predicted from elemental analysis and IR spectroscopy. Thermal decomposition gave supporting evidence for the predicted structure.

INTRODUCTION

Recently we have reported a thermogravimetric study on the dehydration and decomposition of metal complexes derived from hydroxy and phenolic acids [1–6]. A novel thermal feature is observed during the thermal decomposition of $Tl(III)$ –mandelate. In contrast to lactate and glycolate complexes of $Tl(III)$, which undergo single step decomposition, successive decarboxylation was observed for $Tl(III)$ –mandelate. The present communication deals with the same.

The preparation and characterisation of $Tl(III)$ –mandelate was made through elemental analysis, IR spectra and TG, DTG and DTA studies. Attempts have also been made to estimate kinetic parameters for the overall thermal decarboxylation. This has been achieved employing various computational methods, e.g., see Horowitz and Metzger [7], Freeman and Carroll [8], Coats and Redfern [9], and Fuoss et al. [10].

The literature has shown that attempts such as this have not been reported so far.

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MATERIALS AND METHODS

Preparation of Tl(III)-mandelate

All the reagents used were of BDH AnalR grade. Tl(III)-mandelate was prepared by the method as described by Khadikar and Saxena [11]. Freshly precipitated $\text{Tl}(\text{OH})_3$ is added to 1.0 M mandelic acid solution until no more of it dissolves. The solution is digested on a water bath for 3–4 h, when the complex starts separating. The contents are cooled, filtered and washed with ethanol-ether mixture (1 : 1 v/v) and dried in vacuum.

Elemental analysis

The composition of the complex, $\text{Tl}(\text{MAN})_3$, where MAN stands for the anion of mandelic acid, was established by analysing Tl(III) iodometrically [12] and by the elemental analysis of carbon and hydrogen. The carbon and hydrogen were found to be 39.55 and 3.25%, respectively (required: C = 40.56% and H = 3.38%). The Tl(III) estimated was found to be 32.15% (calculated: 32.89%).

IR spectra

The IR spectra of mandelic acid and its Tl(III) complex were recorded on a Pye Unicam SP 1100 recording IR spectrophotometer. The samples were

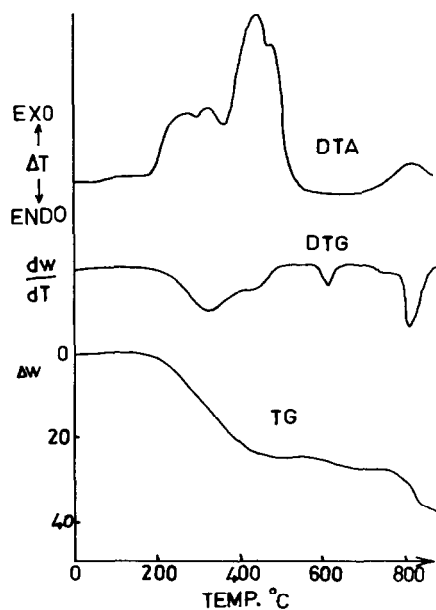


Fig. 1. TG, DTG and DTA curves for tris(mandelato)-thallium(III) complex.

analysed as KBr discs. The exact position of the peak was checked by expansion of the peaks.

Thermal analyses

Thermogravimetry (TG) for 100.0 mg of the sample was carried out on a Stanton-Redcroft recording thermobalance (HT model) of 1.0 mg sensitivity in static air with a heating rate of $4^{\circ}\text{C min}^{-1}$. The chart speed was maintained at 3 in. h^{-1} . The sample was homogenised by sieving below 100 mesh and was packed as uniformly as possible in a platinum crucible of appropriate size.

A differential thermal analysis (DTA) assembly with F and M scientific 240 Hewlett-Packard temperature programmer, and a Platinel-II thermocouple (Engelhard, U.S.A.) was used. The DTA curve for 40.0 mg of the sample was recorded by a Rikadenki Kogyo recorder in static air at a heating rate of $4^{\circ}\text{C min}^{-1}$. Alumina was used as a standard reference material.

The TG, DTG and DTA results are shown in Fig. 1.

RESULTS AND DISCUSSION

Stoichiometry and structure of Tl(III)-mandelate

The results of the elemental analyses indicate that the complex formed between Tl(III) and mandelic acid (MAN) has the composition $\text{Tl}(\text{MAN})_3$. The stoichiometry of the complex has been confirmed by Job's method [13] employing a conductometric technique. Earlier reported data [14] on the solution studies also indicate the formation of a 1 : 3 (Tl:MAN) complex. No conductivity or NHR spectrum of the complex could be measured because of its low solubility in the usual solvents. The complex is stable at room temperature and insensitive to air thus making the handling and kinetic measurements very easy.

IR Spectra

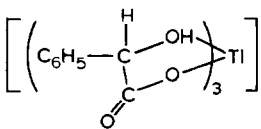
The bonding in Tl(III)-mandelate is discussed by comparing its IR spectrum with that of mandelic acid. The important IR bands of diagnostic value are those of the carboxylate and hydroxyl bands. The IR spectrum of mandelic acid shows a $\nu\text{COO}(\text{asym})$ peak at 1630 cm^{-1} which is indicative of free carboxyl group [15]. Upon coordination of mandelic acid to Tl(III), a shift in this peak to lower frequency (1510 cm^{-1}) was observed. This band was interpreted by Bailar and Bush [16] and by Kirschner [17] as being due to a coordinated carboxylate group. It was thus concluded that the carboxylate group of mandelic acid is coordinated to the Tl(III) in the complex. The

lowering of carboxylate group frequency further indicates that not only is the carboxylate group involved in complexation but also that the extent of ionic or partly covalent character and the carboxylate resonance is maintained. The $\nu\text{COO}(\text{sym})$ in the complex was observed at 1510 cm^{-1} .

Trends in the positions and separation between $\nu\text{COO}(\text{asym})$ and $\nu\text{COO}(\text{sym})$ bands provide useful observations for assigning the coordination type of carboxylate group [18]. The observed $\nu\text{COO}(\text{sym})$ band at 1510 cm^{-1} may be assumed to be strongly indicative of the bridging bidentate nature of carboxylate group.

Comparing the C–O stretching frequencies of the secondary alcoholic group of mandelic acid with Tl(III)–mandelate, it is observed that the former appears as a sharp peak at 1365 cm^{-1} while the latter appears at 1340 cm^{-1} . This is an expected result because the coordination of the oxygen of the hydroxyl group of mandelic acid to Tl(III) ion will reduce its C–O stretching frequency. It may also be noted that the O–H bending peak at 1430 cm^{-1} remained almost at the same position for both mandelic acid and its thallium(III) complex. This shows that there is no loss of proton by the O–H group upon coordination.

By analogy with Tl(III)–lactate [19] and glycolate [20,21] the following structure may be assigned to tris(mandelato)–thallium(III) complex.



Thermal behaviour of Tl(III)–mandelate

The combined TG, DTG and DTA curves for Tl(III)–mandelate are presented in Fig. 1.

Perusal of Fig. 1 shows that the complex starts decomposing at 408 K and the decomposition is followed in three successive steps overlapping each other and without the formation of any stable and isolable intermediate. The decomposition is completed at 1003 K, as shown by a peak in the DTG curve.

The novel feature of the decomposition is that the decarboxylation of the complex takes place in succession (Tables 1 and 2). The observed weight loss (TG) in the first step (523–773 K) indicates the loss of a mandelate moiety. In the following steps II (823–998 K) and step III (1000–1173 K) the remaining two mandelate moieties are lost one after the other. The observed and calculated weight loss for these steps differ slightly. This indicates overlapping stepwise thermal decarboxylation of Tl(III)–mandelate. The corresponding Tl(III) complexes of lactic and glycolic acids [19,20], on the other hand, decompose in a single step. This novel thermal decarboxylation

TABLE 1

Thermal analytical data for Tl(III) complexes of lactic, glycolic and mandelic acids

Complex ^a	DS ^b	Temp. range (K)	Composition of the residue	% Weight loss	
				Calc.	Obs.
Tl(LA) ₃	I	648– 923	Tl ₂ O ₃ /Tl ₂ O/Tl/2Tl ₂ O ₃ ·Tl ₂ O	56.64	55.15
Tl(GLY) ₃	I	625– 923		52.39	52.27
Tl(MAN) ₃	I	523– 773	Tl(MAN) ₂	22.96	20.20
	II	823– 998	Tl(MAN)	45.94	52.20
	III	1000–1173	Tl ₂ O ₃ /Tl ₂ O/Tl/2Tl ₂ O ₃ ·Tl ₂ O	68.90	65.25

^a LA = Lactic acid moiety, GLY = glycolic acid moiety, MAN = mandelic acid moiety.^b DS = Decomposition step(s).

of Tl(III)–mandelate may be attributed to the steric hindrance of the phenyl group of the mandelate moiety.

Another interesting feature of the decomposition is that each of the decomposition steps is accompanied by an exothermic reaction. This is indicated by the exothermic peaks observed at 573, 923 and 1085 K, respectively in the DTA curve. In the thallium(III) complexes of lactic and glycolic acids, on the other hand, the decomposition is followed with an endothermic reaction. This peculiar behaviour of Tl(III)–mandelate may again be attributed to the presence of a phenyl group. The decomposition of the thallium(III) complex through its carbonate should always be an endothermic reaction. The oxidation, however, of a product of cracking from the preceding decomposition process, or that of carbon, may produce an exothermic effect shown on the DTA curve.

It is worth noting that the complex decomposes through the formation of Tl₂(CO₃)₃. However, the final weight loss does not correspond to any of the

TABLE 2

TG horizontal, maxima and range of DTG and DTA peaks of Tl(III) complexes of lactic, glycolic and mandelic acids

Complex ^a	DS ^b	Range of TG horizontal (K)	Maxima of DTG trace (K)	Range of DTG effect (K)	Maxima on DTA trace (K)	Range of DTA effect (K)
Tl(LA) ₃	I	625– 923	873	523– 993	808(s) endo	625– 930
Tl(GLY) ₃	I	648– 923	820	598– 948	843(s) endo	610– 960
Tl(MAN) ₃	I	523– 775	598	463– 608	533(s) exo	498– 583
	II	823– 998	923	623– 773	598(s) exo 713(s) exo	590– 623 673– 733
	III	1000–1173	1093	1163–1203	1123(s) exo	1063–1133

^a LA = Lactic acid moiety, GLY = glycolic acid moiety, MAN = mandelic acid moiety.^b DS = Decomposition step(s).

possibilities such as the formation of $Tl_2O_3/Tl_2O/Tl/2Tl_2O_3 \cdot Tl_2O$. This is in accordance with the observation made by Duval [22]. Accordingly, the non-correspondence of final weight loss is because of the abnormal behaviour of thallium metal in that it possesses volatilisation properties followed by a sublimation process in the region of 900 K.

Kinetic parameters for decarboxylation

Taking into account the complexity of the thermal decomposition of Tl(III)–mandelate, kinetic parameters for the thermal decarboxylation of the third step have been evaluated employing the aforementioned computational methods. However, the kinetic parameters for steps I and II could not be completed due to the absence of an exact inflection point, because the steps overlapped due to rapid thermal decarboxylation.

Order of reaction

The order of reaction, n , was obtained using the following equation suggested by Horowitz and Metzger [7]

$$C_s = n^{1/1-n}$$

where C_s is the weight fraction of the substance present at the DTG peak temperature, T_s ; C_s is given by

$$C_s = \frac{W - W_t^f}{W_0 - W_t^f}$$

where W = weight at the temperature T_s , W_t^f = final weight and W_0 = initial weight of the substance. The order of decomposition of Tl(III)–mandelate is obtained by comparing the C_s value given by the above method with the values given in the Horowitz and Metzger [7] table. The order of reaction is calculated to be one.

The order of decarboxylation as estimated graphically using the Freeman and Carroll method [8], as discussed below, was also found to be one.

Activation energy (E^) and pre-exponential factor (Z)*

Fuoss method

For first order kinetics the method of Fuoss et al. [10] is employed to evaluate the activation energy, E^* , and pre-exponential factor, Z , using the expressions (1) and (2)

$$E^* = \frac{R/T_i^2}{W_i} \left(\frac{dW}{dT} \right)_i \quad (1)$$

$$Z = \frac{a}{W_i} \left(\frac{dW}{dT} \right)_i \exp(E^*/RT_i) \quad (2)$$

TABLE 3
Coats-Redfern treatment for thallium(III)-mandelate

T (K)	$\alpha \times 10^3$	$(T^{-1}) \times 10^3$	$-\log[-\log(1-\alpha)/T^2]$
1023	0.090	0.977	8.059
1033	25.000	0.968	7.625
1043	52.272	0.958	7.307
1053	102.270	0.949	7.012
1063	168.183	0.940	6.788
1073	272.725	0.932	6.558
1083	431.870	0.923	6.317
1093	672.725	0.915	6.029
1103	818.188	0.906	5.853
1113	909.092	0.898	5.713
1123	965.905	0.890	5.572

where T_i = inflection temperature (K), W_i = weight at the point on the TG curve where it goes from concave-down to concave-up, a = heating rate and $(dW/dT)_i$ = rate of change in weight at the point of inflection.

Coats-Redfern method

The Coats-Redfern relation [9] was also employed in the following form (suitable when $n = 1$, as in the present case)

$$-\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{ZR}{\phi E^*} - \frac{E^*}{2.303RT} \quad (3)$$

Here $C = W_{0c} - W/W_{0c}$; W_{0c} = total mass loss for the particular stage; W = mass loss at temperature T (K); Z = pre-exponential factor; R = gas constant; and ϕ = heating rate in K s^{-1} . Plotting $-\log[-\log(1-\alpha)/T^2]$ against T^{-1} (Table 3, Fig. 2) gave a linear plot from which E^* and Z were estimated from the slope and intercept, respectively.

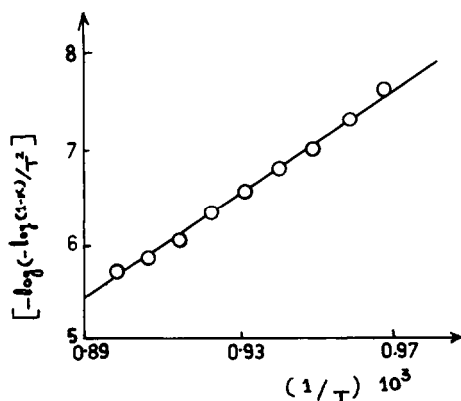


Fig. 2. Coats-Redfern treatment for tris(mandelato)-thallium(III) complex.

TABLE 4

Horowitz–Metzger treatment for thallium(III)–mandelate

T (K)	θ	W_0/W	$\log \log(W_0/W)$
1023	-60	1.009	-4.696
1033	-50	1.026	-3.676
1043	-40	1.055	-2.925
1053	-30	1.114	-2.227
1063	-20	1.202	-1.692
1073	-10	1.375	-1.144
1083	0	1.760	-0.570
1093	+10	3.056	+0.111
1103	+20	5.500	+0.533
1113	+30	11.000	+0.875
1123	+40	29.333	+1.217

Horowitz–Metzger method

This method [7] is most commonly used for the determination of E^* and Z . The expressions used for this purpose are as follows:

$$\ln \ln \frac{W_0}{W} = E\theta/RT_s^2 \quad (4)$$

$$\ln \frac{W}{W_0} = -\frac{Z}{q} \frac{RT_s^2}{E^*} \exp(-E/RT_s) \quad (5)$$

Here W_0 = initial weight; W = weight remaining at a given temperature; T_s = reference temperature at which dW/dT is a maximum and $\theta = T - T_s$ (Table 4). A plot of $\ln \ln(W_0/W)$ vs. θ gives a straight line (Fig. 3). E^* and Z are then obtained from the slope and intercept, respectively.

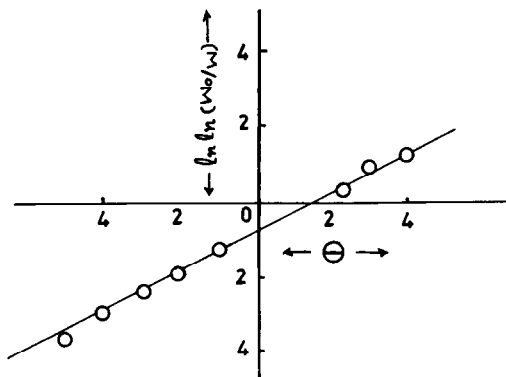


Fig. 3. Horowitz–Metzger treatment for tris(mandelato)–thallium(III) complex.

TABLE 5

Freeman-Carroll treatment for thallium(III)-mandelate

T (K)	$\Delta(1/T) \times 10^3$	W_r	$\Delta \log W_r \times 10^3$	$\Delta \log dW/dT \times 10^3$	$\frac{\Delta \log(dW/dT)}{\Delta \log W_r}$	$\frac{(1/T) \times 10^3}{\log W_r}$
1023	0.0097	10.905	3.96	-301.93	-76.017	2.449
1033	0.0095	10.725	7.03	-96.91	-13.785	1.351
1043	0.0092	10.425	12.32	-297.70	-24.164	0.747
1053	0.0091	9.875	23.55	-211.95	-9.392	0.386
1063	0.0090	9.510	33.11	-188.72	-5.699	0.272
1073	0.0087	8.000	58.33	-140.82	-2.474	0.149
1083	0.0086	6.250	107.21	-100.81	-1.499	0.080
1093	0.0085	3.655	239.58	+119.18	+0.497	0.035
1103	0.0083	2.000	255.27	+235.36	+0.929	0.032
1113	0.0081	1.000	301.03	+196.30	+0.652	0.027
1123	0.0080	0.375	425.96	+243.04	+0.570	0.018

Freeman-Carroll method

According to Freeman and Carroll [8], a plot of $\Delta \log(dW/dT)/\Delta \log W_r$ against $\Delta(1/T)/\Delta \log W_r$ should yield a straight line. The slope gives E^*/R and the intercept at the y -axis gives the value of n . Large experimental scatter in the plot is obviated by reading dW/dT from the TG curve. Here, W = weight loss at temperature T (K); W_c = total weight loss; and $W_r = W_c - W$ (Table 5).

The expression correlating n with E^* is as follows

$$-\frac{E^*/R \Delta(1/T)}{\Delta \log W_r} = -n + \Delta \log(dW/dT)/\Delta \log W_r \quad (6)$$

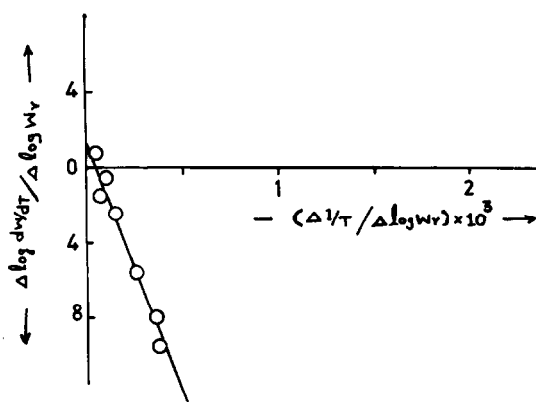


Fig. 4. Freeman-Carroll treatment for tris(mandelato)-thallium(III) complex.

TABLE 6

Kinetic parameters for the thermal decarboxylation of Tl(III)-mandelate, lactate and glycolate ^a

Complex	Method	T_i (K)	E^*	S^*	Z^*	K_r
Tl(III)-mandelate	I	1023	120.40	-2.72	5.84×10^{21}	5.20×10^{-3}
	II	1023	120.65	-2.65	6.01×10^{21}	6.25×10^{-3}
	III	1023	120.20	-	9.38×10^{21}	5.16×10^{-3}
	IV	1023	120.98	-2.78	-	-
Average		1023	120.56	-2.72	7.08×10^{21}	5.54×10^{-3}
Tl(III)-lactate	I	813	63.04	-3.23	2.32×10^{14}	2.68×10^{-3}
	II	813	63.06	-3.25	2.93×10^{14}	2.52×10^{-3}
	III	813	63.36	-3.14	2.20×10^{14}	2.22×10^{-3}
	IV	813	63.16	-	-	-
Average		813	63.16	-3.21	2.48×10^{14}	2.47×10^{-3}
Tl(III)-glycollate	I	833	67.01	-3.60	1.42×10^{15}	3.75×10^{-3}
	II	833	67.09	-3.24	3.06×10^{15}	3.74×10^{-3}
	III	833	66.78	-3.82	1.11×10^{15}	3.50×10^{-3}
	IV	833	67.22	-	-	-
Average		833	67.03	-3.55	1.86×10^{15}	3.60×10^{-3}

^a I = Horowitz-Metzger method; II = Coats-Redfern method; III = Fuoss method; IV = Freeman-Carroll method; E^* = activation energy (kcal mol⁻¹); H^* = activation enthalpy (kcal mol⁻¹); S^* = activation entropy (e.u.); G^* = free energy of activation (kcal mol⁻¹); Z = frequency factor (s⁻¹); K_r = specific reaction rate (s⁻¹).

The values of E^* and n obtained from the plot of

$$\frac{\Delta \log(dW/dT)}{\Delta \log W_r}$$

against $\Delta(1/T)/\Delta \log W_r$ (Fig. 4) are presented in Table 6.

Evaluation of other kinetic parameters

Activation entropy, S^* , free energy of activation, G^* , and the specific reaction rate constant, K_r , have been calculated using their interrelationships [23] given in eqns. (7-9), respectively

$$S^* = (\log Zh/kT)R \quad (7)$$

$$G^* = E^* - T_i S^* \quad (8)$$

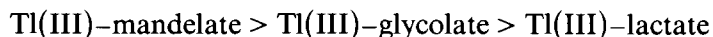
$$K_r = Z \exp(-E^*/RT_i) \quad (9)$$

In eqn. (7), k and h are the Boltzmann and Planck constants, respectively.

The kinetic parameters thus obtained are presented in Table 6. Earlier reported values of kinetic parameters for Tl(III) complexes of lactic [20] and glycolic acid [19] are also reported for comparison.

Perusal of Table 6 shows that the activation energy, E^* , for the decarboxylation of Tl(III)-mandelate lies around $120 \text{ kcal mol}^{-1}$, with an estimated uncertainty of $\pm 0.5 \text{ kcal mol}^{-1}$. The values are comparable with the generally accepted values for activation energy of the decarboxylation reaction [24,25].

It is interesting to compare the activation energy of thermal decarboxylation of Tl(III)-mandelate with those of lactate and glycolate. The values reported in Table 6, follow the order of activation energy given as:



This indicates that the M-O bond is strongest in Tl(III)-mandelate, which is clearly the case as shown from its stepwise decarboxylation.

It is notable that the rate of thermal decomposition cannot be determined solely by the energy of activation, E^* , since the frequency factor (Z) can vary over a considerable range. It is the free energy of activation, G^* , which determines the rate of reaction at a given temperature [26]. The higher the value of G^* , the slower is the reaction at a given temperature. Table 6 shows that the G^* value also varies in the order of energy of activation.

The enthalpy of activation, H^* , has been evaluated from the relationship:

$$H^* = E^* - RT_1 \quad (10)$$

The values of E^* and H^* differ by an average of $1.00 \text{ kcal mol}^{-1}$. This small difference could not be differentiated experimentally and we can safely say that E^* and H^* are equivalent. The error limit in the values of H^* is $\pm 0.5 \text{ kcal mol}^{-1}$.

The results presented in Table 6 are within the range usually observed for a first order reaction [24-26]. Thus it can be concluded that the thermal decarboxylation of Tl(III)-mandelate follows first order kinetics.

If the entropy of activation S^* , is negative, the activated complex is less probable and the rate is slower. Thus the large negative value of entropy of activation and high free energy of activation means a slow reaction. The magnitude of the negative entropy of activation in the case of Tl(III)-mandelate suggests that the thermal decarboxylation is lower compared to that of Tl(III)-lactate and glycolate. This is clearly borne out from the shape of the corresponding TG curve.

It is worth noting that the kinetic parameters obtained from the different methods are close to each other. Such a good agreement could only be attributed to coincidence, because there are several steps involved in obtaining the final results, and each step could give rise to some error; e.g., error in curve fitting or slope measurements. Unless some errors happen to cancel each other by chance, it is impossible to obtain such a good agreement.

CONCLUSION

Unlike single step endothermal decarboxylation of tris(lactato)- and tris(glycolato)-thallium(III) complexes, the decarboxylation of tris(mandelato)-thallium(III) complex is a multistep exothermal reaction. This novel behaviour of the mandelato complex of Tl(III) may be attributed to the presence of a phenyl (C_6H_5) moiety in mandelic acid. The stepwise thermal decarboxylation further indicates that the M-O bond is stronger in mandelato as compared to lactato and glycolato complexes of Tl(III). Observed parameters support this view.

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