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THERMAL DECOMPOSITION OF THE MALATO-AQUO COMPLEX OF THALLIUM(III): THE MECHANISM OF THERMAL DEHYDRATION OF THALLIUM(III) MALATE TRIHYDRATE

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ABSTRACT

The thermal dehydration of $Tl(MAL) \cdot 3H_2O$, where MAL stands for the anion of malic acid and Tl for thallium in the trivalent state, was studied by thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) techniques. The results show the release of all three water molecules in a single step, indicating their identical bonding features. The IR spectra of the ligand and the complex indicate the bidentate character of the carboxylate ion and, in addition, that the protons from the hydroxyl group are not replaced during complex formation. The dehydrated species loses a water molecule forming thallium(III) maleate and the decomposition is complete with Tl_2O_3 as the end product. The various kinetic parameters were estimated by employing several computational methods. Refined values were then obtained by regression analysis of the data derived from the various methods used.

INTRODUCTION

Recently, we have reported the thermal dehydration and decomposition of metal complexes of salicylic acid and nuclear substituted salicyclic acids [1–6]. Work on the thermal decomposition of metal complexes of hydroxy acids is very limited. In addition, work on the thermal decomposition of heavy metal carboxylates has started only recently [7–9]. As an extension of previous efforts [1–6], this report deals with the thermal dehydration of Tl(III) malate. The mechanism of decomposition and the nature of the decomposition products are studied. As yet attempts such as this have not been made. The preparation and characterization of Tl(III) malate was carried out using elemental analysis, IR spectroscopy, thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) studies. Attempts were also made to estimate kinetic parameters from thermal studies by employing various computational methods, e.g.

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those of Horowitz and Metzger [10], Freeman and Carroll [11], Coats and Redfern [12] and Fuoss et al. [13]. Finally, refined values for the various kinetic and thermodynamic parameters were obtained by the regression analysis of data using the least-squares method.

MATERIALS AND METHODS

Preparation of Tl(III) malate

All chemicals used were of AnalaR grade (BDH).

Tl(III) malate was prepared as reported earlier [14]. Freshly precipitated $Tl(OH)_3$ was added to a one-molar solution of malic acid until no more dissolved. The solution was digested in a water bath for 3–4 h to separate the complex. The solution was placed in an ice bath to ensure complete precipitation. The neutral complex was isolated by filtration, washed with water, ethanol and diethyl-ether and dried in vacuum over $CaCl_2$.

Elemental analyses

The composition of the Tl(III) malate, $Tl(MAL) \cdot 3H_2O$, where MAL stands for the anion of malic acid, was determined by analysing thallium iodometrically [15] and by microanalysis of carbon and hydrogen. Carbon and hydrogen found: C, 12.37% and H, 2.45%; calculated: C, 12.29% and H, 2.56%. The sample taken for thermal studies was homogenized by sieving below 100 mesh.

IR measurements

Infrared absorption spectra (KBr discs) were obtained with a Perkin Elmer infrared spectrophotometer, model 257. The exact position of the peaks was checked by expansion of the peaks.

Thermal analyses

Thermogravimetry of a 100.0 mg sample was carried out on a Stanton Redcroft recording thermobalance (HT model) in static air with a heating rate of 4 °C min^{-1} (with a sensitivity of 1 mg). The chart speed was maintained at 3 in h^{-1}. The sample was packed as uniformly as possible in a platinum crucible of appropriate size.

A DTA assembly with an F and M Scientific 240 Hewlett Packard temperature programmer and a Platinel-II thermocouple (Engelhard, U.S.A.) was used. The DTA curve for a 40.0 mg sample was recorded by a

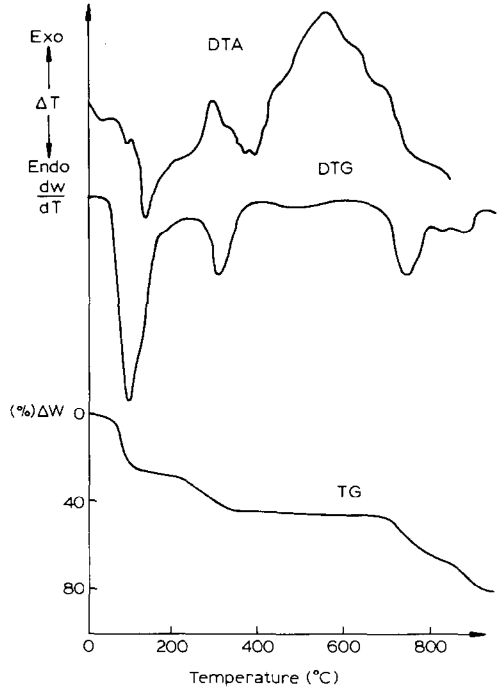


Fig. 1. TG, DTG and DTA curves for thermal decomposition of thallium(III) malate.

TABLE 1

TG, DTG and DTA data for the malato-triaquo thallium(III) complex [a,e]

Step	Process	TG data			DTA data		
		Temp. range (°C)	Residue (%)		Temp. range (°C)	Peak temp. (°C)	Peak nature [b]
			Found	Calculated			
I	$(C_4H_4O_5)Tl \cdot 3H_2O$ $\rightarrow (C_4H_4O_5)Tl$	100–220	77.78	76.25	80–200	200	Endo
II	$(C_4H_4O_5)Tl$ $\rightarrow (C_4H_2O_4)Tl$	220–300	70.38	69.65	250–330	275 [d]	Endo [c]
III	$(C_4H_2O_4)Tl$ $\rightarrow Tl_2(CO_3)$ $\rightarrow Tl_2O_3$	300–675	22.64	20.75	675–900	725 [d]	Exo [c]

[a] Each value is a mean of three determinations.

[b] Endo = endothermic, exo = exothermic.

[c] Processes are defined by more than one peak indicating the multistep decomposition, favouring the formation of Tl(III) maleate.

[d] In the multistep case, the first peak temperature is of principal consideration.

[e] Elemental analysis: %Tl, 57.70 (52.35); %C, 12.37 (12.29); %H, 2.45 (2.56). The calculated values are given in parentheses.

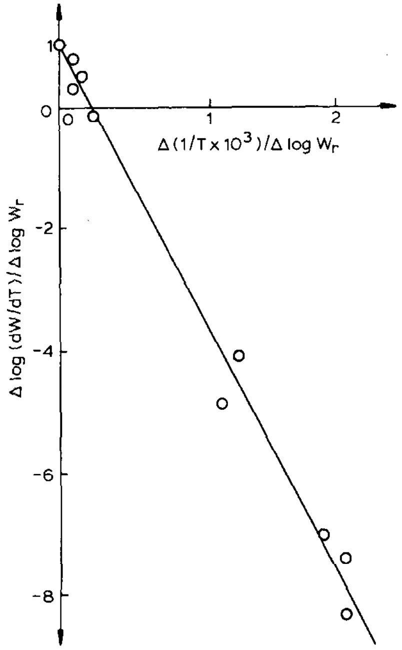


Fig. 2. Freeman and Carroll treatment for thallium(III) malate.

Rikadenki Kogyo recorder in static air at a heating rate of 4°C min^{-1}. Alumina was used as a standard reference material.

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

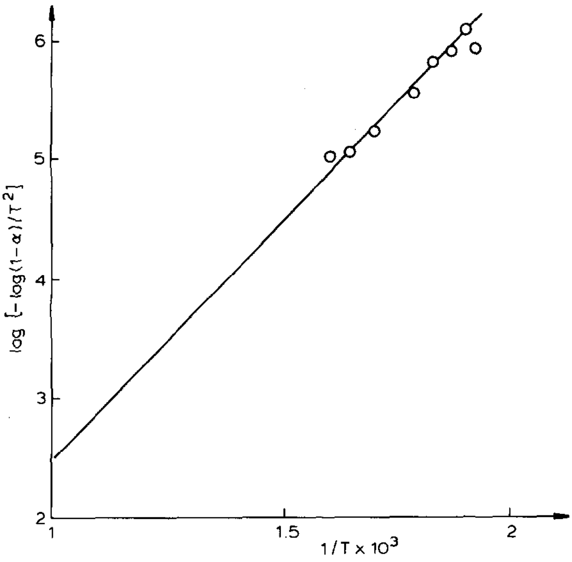


Fig. 3. Coats and Redfern treatment for thallium(III) malate.

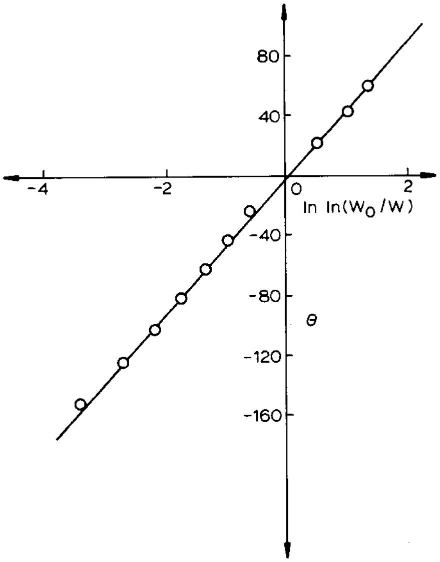


Fig. 4. Horowitz and Metzger treatment for thallium(III) malate.

Presentation of the data

Various observations made in the present investigation are presented in Figs. 1–4 and are summarized in Tables 1–6. In Table 1 the range of thermal decomposition, the residue left during specific stages of decomposition, the corresponding DTA temperature range and the nature of the DTA peaks (exo or endo) are given. All this information is derived from Fig. 1.

The results obtained using the treatments of Freeman and Carroll [11], Coats and Redfern [12] and Horowitz and Metzger [10] are given in Figs. 2, 3 and 4 respectively. The corresponding data needed for the estimation of various kinetic parameters from these methods are given in Tables 2–4, respectively.

TABLE 2

Freeman and Carroll [11] treatment for the thermal dehydration of $Tl(MAL)\cdot 3H_2O$

Step no.	Temp. (K)	$\Delta(1/T \times 10^3)$	$\Delta \log_{10} W_r$	$\Delta \log_{10} (dW/dt)$	$\dfrac{\Delta \log_{10}(dW/dT)}{\Delta \log_{10} W_r}$	$\dfrac{\Delta(1/T \times 10^3)}{\Delta \log_{10} W_r}$
1	503	0.0823	0.03502	−0.29776	−8.502	2.350
2	523	0.0760	0.04908	−0.19640	−4.001	1.548
3	543	0.0740	0.05535	−0.26895	−4.857	1.272
4	563	0.0655	0.22045	−0.06624	−0.300	0.297
5	583	0.0609	0.49136	+0.47710	+0.971	0.124
6	603	0.0569	0.45593	+0.27353	+0.599	0.125
7	623	0.0532	0.54407	+0.21762	+0.400	0.098

TABLE 3

Coats and Redfern [12] treatment for the thermal dehydration of Tl(MAL)·3H_2O

Step no.	Temp. (K)	α	$1/T \times 10^{-3}$	$\log_{10}[-\ln(1-\alpha)/T^2]$
1	503	0.22941	1.9880	5.987
2	523	0.31176	1.9120	5.865
3	543	0.39411	1.8416	5.770
4	563	0.63529	1.7762	5.497
5	583	0.88235	1.7153	5.201
6	603	0.95882	1.6584	5.057
7	623	0.98823	1.6051	4.941

TABLE 4

Horowitz and Metzger [10] treatment for the thermal dehydration of Tl(MAL)·3H_2O

Step no.	Temp. (K)	θ	$\ln \ln(W_0/W)$
1	423	−140	−3.511
2	443	−120	−2.705
3	463	−1100	−2.133
4	483	−80	−1.715
5	503	−60	−1.345
6	523	−40	−0.985
7	543	−20	−0.691
8	563	0	+0.0086
9	583	+20	+0.761
10	603	+40	+1.160
11	623	+60	+1.491

TABLE 5

Least-square command for the data obtained for the thermal dehydration of Tl(MAL)·3H_2O from the methods of Freeman and Carroll, Horowitz and Metzger and Coats and Redfern

Step no.	Parameters	Computational methods		
		Freeman and Carroll	Horowitz and Metzger	Coats and Redfern
1	n	7	11	7
2	Σx	5.81	−440	12.49
3	Σy	−15.69	9.66	38.31
4	Σx^2	9.80	61600	22.42
5	Σy^2	113.43	34.53	210.78
6	Σxy	−32.20	1451.5	68.74
7	$(\Sigma x)^2$	33.80	193600	156.16
8	$(\Sigma y)^2$	246.17	93.40	1468.26
9	R	0.972	0.993	0.998

TABLE 6

Kinetic and thermodynamic parameters for the thermal dehydration of $Tl(MAL) \cdot 3H_2O$ [a]

Step no.	Method [b]	T_s (K)	$E^\star$ (kcal mol^{-1})	$G^\star$ (kcal mol^{-1})	$H^\star$ (kcal mol^{-1})	$\log_{10} k$ (s^{-1})	$\log_{10} z$ (s^{-1})	$S^\star$ (e.u.)
1	Horowitz and Metzger	485.5	19.56(18.27)	27.71(26.42)	18.60(17.30)	4.53(4.52)	4.54	−16.80(16.80)
2	Freeman and Carroll	485.5	17.24(17.43)	–	16.28(16.46)	–	–	–
3	Coats and Redfern	485.5	17.51(17.72)	25.60(25.80)	16.54(16.75)	4.60(4.60)	4.62(4.62)	−16.66(16.66)
4	Average values	485.5	18.10(17.80)	26.655(26.11)	17.14(16.836)	4.565(4.56)	4.58	−16.73

[a] $E^\star$ = energy of activation (kcal mol^{-1}); $G^\star$ = free energy of activation (kcal mol^{-1}); $H^\star$ = enthalpy of activation (kcal mol^{-1}); Z = frequency factor; k = specific rate constant; $S^\star$ = enthalpy of activation.

[b] Values in parentheses were obtained from the regression analysis of the data.

The precise values for the various kinetic and thermodynamic parameters were then calculated by the regression analysis of the data obtained from the computational methods mentioned above. The least-square commands for these methods are summarized in Table 5.

Finally, the computed parameters are given in Table 6.

RESULTS AND DISCUSSION

Composition and structure

The results of the elemental analyses indicate 1 : 1 stoichiometry for the complex formed between Tl(III) and malic acid. It has the composition $Tl(MAL) \cdot 3H_2O$ where MAL stands for the anion of malic acid. No conductivity or nuclear magnetic resonance (NMR) 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 kinetic measurements very easy.

The Tl(III) ion under investigation is capable of extending its coordination number to six. Therefore the appearance of IR bands at 1620, 850 and 525 cm^{-1} indicates the presence of coordinated water [16]. The bands are assigned to $\delta(OH)$, $\delta(H_2O)$ and $\pi(H_2O)$ modes of coordinated water [16–21]. This is further borne out by the thermal decomposition data (Fig. 1, Table 1).

The important IR bands of diagnostic value are those of carboxylate and hydroxyl and bands due to coordination of water molecules. In the carboxylato complexes symmetrical (γCOO(sym)) and asymmetrical (νCOO(asy)) stretching modes of the COO group are of great importance, since their positions and separation can help in the determination of the type of bonding.

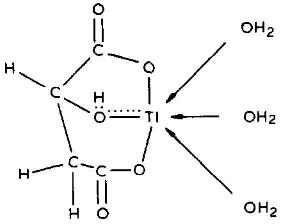
The IR spectrum of malic acid shows a νCOO(asy) peak at 1740 cm^{-1} which is indicative of free carboxyl groups [21]. Upon coordination of malic acid to Tl(III), a shift in the peak to lower frequency (1612 cm^{-1}) was observed. This band was interpreted by Bush and Bailar [22] and by Kirschner [23] as being due to a coordinated carboxylate group. It was thus concluded that the carboxylate group of malic acid is coordinated to the Tl(III) ion in the complex.

The symmetric carboxylate stretching frequency in the complex was observed at 1570 cm^{-1}. The difference (170 cm^{-1}) between the νCOO(asy) and νCOO(sym) frequency indicates the bidentate character of the carboxylate group [24].

When comparing the C–O stretching frequencies of the secondary alcoholic group of malic acid and Tl(III) malate, it is observed that a sharp peak appears at 1370 cm^{-1} for the former and at 1345 cm^{-1} for the latter.

This is an expected result because the coordination of the oxygen of the hydroxyl group of malic acid to the 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} is at almost the same position for both malic acid and its Tl(III) complex. This shows that protons from the alcoholic OH group are not lost upon coordination.

By analogy with In(III) lactate [25] and Tl(III) glycolate [26], we expect the malate complex of Tl(III) to have the following structure



Thermal decomposition would appear to be consistent with this type of structure and would suggest that the water molecules are directly bonded to the Tl(III) ion along with one ligand moiety to give a coordination number of six for the Tl(III) ion.

Thermal study of Tl(III) malate

The combined TG, DTG and DTA curves of a sample of Tl(III) malate are given in Fig. 1.

The decomposition of the complex begins at about 373 K and is complete at 950 K, as shown by a peak in the DTG curve. An examination of the TG curve indicates that Tl(III) malate is stable up to 363 K and beyond this temperature, dehydration occurs with the elimination of three water molecules to form a dehydrated product. Subsequently, the dehydrated product loses a water molecule forming Tl(III) maleate as can be seen from the observed percentage weight loss of 70.38% (calculated 69.65%). Finally, decomposition is complete forming Tl_2O_3 as the end product. The dehydration is complete at 493 K. The decomposition of the system has a temperature range of 373–950 K with the reaction intervals at 493 and 573 K. The percentage weight of residue remaining (calculated from the TG curve for the thermal dehydration step I) is 76.25% (calculated, 77.78%). This corresponds to the loss of three water moieties. Thus, TG and DTG curves show a two-step decomposition of Tl(III) malate: dehydration, followed by the decomposition of the dehydrated product. The corresponding DTA curve indicates a large endothermic region with peaks at 473 and 548 K.

It is worth noting that the complex decomposes through the formation of $Tl_2(CO_3)_3$. However, the final weight loss does not correspond to any of the likely 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 [27]. This non-correspondence of the final weight loss is due to the abnormal behaviour of thallium metal. Volatilization occurs followed by a sublimation process in the neighbourhood of 900 K.

Kinetic parameters

Various kinetic parameters for the thermal dehydration of Tl(III) malate were evaluated by employing various computational methods, namely, those of Horowitz and Metzger [10], Freeman and Carroll [11], Coats and Redfern [12] and Fuoss et al. [13].

Determination of the order of reaction

The order of reaction n was determined by applying the equation of Horowitz and Metzger $C_S = (n)^{1/1-n}$, where C_S is the weight fraction of the substance present at the peak temperature T_S (the DTG peak temperature). In the present case the order of thermal dehydration was calculated to be unity. The Freeman and Carroll method [11], as described below, was also used for the estimation of the order of reaction. It also indicated the order of reaction to be unity.

Evaluation of other kinetic parameters

The estimation of the other kinetic parameters such as energy ($E^\star$), entropy ($S^\star$) and free energy ($G^\star$) of activation and the pre-exponential factor (Z) were made by employing one or more of the following methods.

Method of Freeman and Carroll [11]. The treatment of Freeman and Carroll is shown in Table 2, and data are plotted in Fig. 2. It is seen from Fig. 2 that the two points at the beginning of the run do not seem to be very accurate. With the exception of the initial three points, the points can be fitted into a straight line; the intercept on the y axis indicates that the order of reaction is unity. From the slope of the straight line an activation energy of 17.24 kcal mol^{-1} was obtained (Table 6).

Method of Coats and Redfern [12]. The treatment of the data by the method of Coats and Redfern is shown in Table 3 with the corresponding plot in Fig. 3. The activation energy $E^\star$ and pre-exponential factor Z are calculated from the slope and the intercept on the y axis, respectively. The values so obtained are presented in Table 6.

Method of Horowitz and Metzger [10]. This method is most commonly used for the estimation of $E^\star$ and Z. Treatment of the data by this method is shown in Table 4 and the results are plotted in Fig. 4. The values of $E^\star$ and Z obtained from the slope and the intercept are given in Table 6.

Method of Fuoss et al. [13]. Fuoss et al. [13] have suggested an expression for the evaluation of $E^\star$ and Z for first-order kinetics. These are calculated using the relationships

$$E^\star = \frac{RT_i^2}{W_i}\left(\frac{\mathrm{d}W}{\mathrm{d}T}\right)_i$$

and

$$Z = \frac{a}{W_i}\left(\frac{\mathrm{d}W}{\mathrm{d}T}\right)_i \exp\left(\frac{E^\star}{RT_i}\right)$$

where the terms have their usual meaning.

The values of $E^\star$ and Z are given in Table 6.

Using the inter-relationship [22] of Z with $S^\star$, the latter is calculated by the relation

$$S^\star = (\log_{10} Z.h/KT_i)R$$

where R and h are the Boltzmann and Planck constants, respectively.

The reaction rate depends mainly on the free energy of activation ($G^\star$); the activation entropy ($S^\star$) should decide the magnitude of $G^\star$ according to the relation

$$G^\star = E^\star - T_i S^\star$$

Finally, the specific rate constant (K_r) is calculated by the relation

$$K_r = Z\exp(-E^\star/RT_i)$$

The parameters $E^\star$, $S^\star$, $G^\star$ and Z calculated from the afore-mentioned methods and relationships are summarized in Table 6.

Regression analysis of the data

In order to obtain precise values of $E^\star$, the data from the various computational methods are subjected to the method of least squares. The high values of the correlation coefficient (γ): 0.998, 0.993 and 0.972 for the Coats and Redfern, Horowitz and Metzger and Freeman and Carroll treatments, respectively, show a very good linearity. The values of $E^\star$ obtained from the regression analysis, in each case, agree well with those obtained directly from the slope of the straight line plot. The uncertainty is ± 1.0 kcal mol^{-1}.

DISCUSSION

A perusal of Table 6 shows that the activation energy ($E^\star$) for the dehydration of Tl(III) malate lies around 18.0 kcal mol^{-1}, with an estimated uncertainty of ± 0.5 kcal mol^{-1}. These values are comparable with the generally accepted values of the activation energy of the dehydration reaction [28,29].

It is worth noting that the activation energies obtained from the Coats and Redfern and the Freeman and Carroll methods are similar to each other. Such a good agreement can 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, for instance, an error in curve fitting and/or an error in slope measurement. Unless some errors happen to cancel each other by chance, it would be impossible to obtain such a good agreement. However, the kinetic parameters derived from the Horowitz and Metzger method are somewhat higher than those obtained from the other two methods. This is in agreement with our recent observations [25,26] as well as those of Fong and Chen [30], Sestak et al. [31] and Ozawa [32].

It should also be noted that the rate of thermal decomposition cannot be determined solely by the energy of activation ($E^\star$), since the frequency factor can vary over a considerable range. It is the free energy of activation ($G^\star$), which determines the rate of reaction at a given temperature [33]. The higher the $G^\star$ value, the slower is the reaction rate at a given temperature. If the entropy of activation ($S^\star$) is negative, the activated complex is less probable and the rate is slower [34]. Thus a large negative entropy of activation and a high free energy of activation denote a slow reaction. The magnitude of the negative entropy of activation in the present case suggests appreciable thermal dehydration of Tl(III) malate. This is clearly borne out from the shape of the TG curve.

The enthalpy of activation $H^\star$ has been evaluated from the relationship

$$H^\star = E^\star - RT_i$$

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

The results presented in Table 6 are within the range usually observed for a first-order thermal dehydration [35]. Thus it can be concluded that the thermal dehydration of Tl(III) malate is a first-order reaction.

Mechanism of thermal decomposition

On the basis of the discussion above the general features of the thermal decomposition can be represented by

$$\mathrm{Tl(MAL)\cdot 3H_2O \rightarrow Tl(MAL) + 3H_2O} \qquad (1)$$

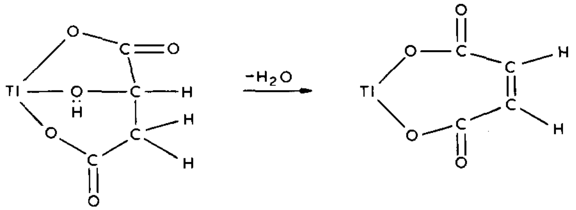
$$\mathrm{Tl(MAL) \rightarrow Tl(MALE) + H_2O} \qquad (2)$$

$$\mathrm{Tl(MALE) \rightarrow Tl_2(CO_3)_3 \rightarrow Tl_2O_3} \qquad (3)$$

where MALE represents the maleate moiety.

The temperature range for reaction (1) is 100–220 °C (Fig. 1, Table 1). There are two overlapping peaks for the loss of three water molecules. This result can be explained by the structure of the complex changing from octahedral to tetrahedral (loss of two water molecules) prior to the loss of the third water molecule.

Reaction (2) occurs in the temperature range 220–300 °C. At this stage an additional water molecule is lost. This probably follows the following reaction



Both the first and second reactions are endothermic.

Reaction (3) is characterized by three exothermic peaks (DTA maxima) suggesting that the decarboxylation of Tl(III) malate is a multistep reaction.

CONCLUSION

Unlike the formation of tris-(hydroxyacid)Tl(III) complexes, malic acid forms only 1 : 1 (Tl : MAL) complexes. This is probably due to the established tridentate nature of the malate moiety. In addition, in other cases [25,26] the decarboxylation occurs either in single or multiple steps during which the ligand molecules are lost without configurational changes. However, in the present case an intermediate Tl(III) maleate is formed and the reaction is equivalent to a ligand substitution process.

Finally, the formation of Tl(III) malate trihydrate and the thermal stability over a wide range suggest that the thermal techniques (TG, DTG and DTA) can be used as probes for the analytical estimation of Tl(III).

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