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STRUCTURE AND THERMAL CHARACTERIZATION OF TRIS-THALLIUM(III) GLYCOLLATE

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The thermal decarboxylation of $Tl(GLA)_3$ (where GLA stands for the anion of glycollic acid) was studied by TG, DTG and DTA techniques. The results showed the escape of all three glycollic acid moieties in a single step. The IR spectra of the ligand and the complex indicated the bidentate character of carboxylate ion and the fact that the proton from the hydroxy group is not replaced during complex formation. The various kinetic and thermodynamic parameters were estimated from analysis of the TG, DTG and DTA curves of the sample, employing several computational methods. Precise results were then obtained by the method of least squares and are discussed.

The thermal decomposition of metal carboxylates has attracted great interest during recent years [1, 2]. However, work on the thermal decomposition of heavy metal carboxylates started only a short time ago [3]. Recently, we reported on the thermal dehydration and decomposition of metal complexes of salicylic and nuclear substituted salicylic acids [4–9]. The work on the thermal decomposition of metal complexes of hydroxy acids is very limited. As an extension of our previous studies [4–9], the present report deals with the thermal decarboxylation of Tl(III) glycollate, with a view to understanding the mechanism of the decomposition and the nature of the decomposition products. The characterization of Tl(III) glycollate was carried out through elemental analysis, IR spectra, TG, DTG and DTA studies. Attempts were also made to estimate the kinetic parameters from thermal studies, employing different computational methods, e.g. the Horowitz–Metzger [10], Freeman–Carroll [11], Coats–Redfern [12] and Fuoss [13] methods. The data obtained were then subjected to the method of least squares.

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Material and methods

Preparation of Tl(III) glycollate

All the chemicals used were of B. D. H. AnalaR grade.

Tl(III) glycollate was prepared as reported earlier [14]. Freshly precipitated $Tl(OH)_3$ was added to a 1 M solution of glycollic acid till no more dissolved. The solution was digested on a water-bath for 3–4 hours, when the complex started to separate out. 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 vacuuo over $CaCl_2$.

Elemental analyses

The composition of the anhydrous sample, $Tl(GLA)_3$, where GLA stands for the anion of glycollic acid, was determined by analysing thallium iodometrically [15] and by microanalysis of carbon and hydrogen. The carbon and hydrogen were found to be 16.66% and 1.98% (calculated: C = 16.77 and H = 2.10), respectively. 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 positions of the peaks were checked by expansion of the peaks.

Thermal analyses

Thermogravimetry (TG) on 100.0 mg of the sample was carried out on a Stanton–Redcroft recording thermobalance (HT model) of 1 mg sensitivity, in static air, at a heating rate of 4 deg min^{-1}. 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 differential thermal analysis (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 40.0 mg sample was recorded with a Rikadenki Kogyo recorder, in static air, at a heating rate of 4 deg min^{-1}. Alumina was used as standard reference material.

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

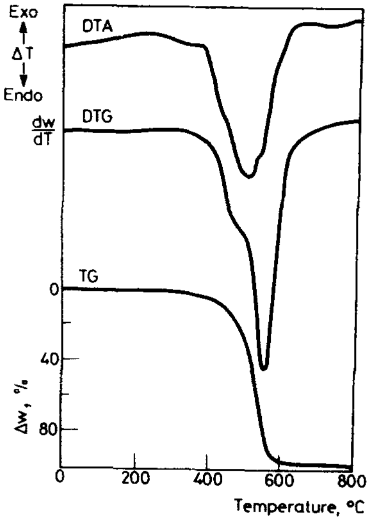


Fig. 1 TG, DTG and DTA curves for tris-thallium(III) glycollate

Results and discussion

Composition and structure

The results of the elemental analyses indicated that the complex formed between Tl(III) and glycollic acid has the composition $Tl(GLA)_3$. No conductivity or 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, thereby making the handling and kinetic measurements very easy.

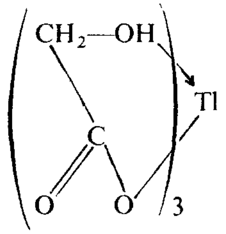
The important IR bands of diagnostic value are those of the carboxylate and hydroxy bands. In the carboxylato complexes, symmetrical (νCOO(sym)) and asymmetrical (νCOO(asy)) stretching modes of the COO group are of great importance, since their positions and separation can help in the determination of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

The IR spectrum of glycollic acid shows a νCOO(asy) peak at 1675 cm^{-1}, which is indicative of free carboxyl groups [16]. Upon coordination of glycollic acid to Tl(III), a shift in the peak to lower frequency (1610 cm^{-1}) was observed. This band was interpreed by Bailar Jr. et al. [17] and by Kirschner [18] as being due to the coordinated carboxylate group. It was therefore concluded that the carboxylate group of glycollic acid is coordinated to the Tl(III) ion in the complex.

The symmetric carboxylate stretching frequency in the complex was observed at 1440 cm^{-1}. The difference Δ (170 cm^{-1}) between the νCOO(asy) and νCOO(sym) frequencies indicates, the bidentate character of the carboxylate group [19].

When the C—O stretching frequencies of the secondary alcoholic OH groups of glycollic acid and Tl(III) glycollate are compared, it is observed that there is a sharp peak at 1370 cm^{-1} for the former, while for the latter the peak lies at 1345 cm^{-1}. This is an expected result, becaue the coordination of the oxygen of the hydroxy group of glycollic 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 1435 cm^{-1} occurred at almost the same position for glycollic acid and its Tl(III) complex. This shows that there is no loss of proton by the alcoholic OH group upon coordination.

By analogy with In(III) lactate [20], we expect the trisglycollato complex of Tl(III) to have the following structure:



Thermal study of Tl(III) glycollate

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

The decomposition of the complex starts at about 623 K and is completed at 863 K, as shown by a peak in the DTG curve. In Table 2, it is seen that $\alpha = 1.00$ at 863 K, which also implies that the reaction is completed at this temperature.

Table 1 Freeman–Carroll treatment for tris-thallium(III) glycollate[a]

Temp., K	$\Delta\left(\frac{1}{T}\right) \times 10^3$	W_r	$\Delta \log W_r \times 10^3$	$\frac{dW}{dT} \times 10^3$	$\frac{\Delta \log \frac{dW}{dT}}{\Delta \log W_r}$	$\frac{\Delta\left(\frac{1}{T} \times 10^3\right)}{\Delta \log W_r}$
773	0.1700	65.50	22.28	20.16	−4.349	0.763
783	0.0165	62.50	26.94	25.20	−15.808	0.612
793	0.0161	57.75	34.33	94.82	−5.582	0.469
803	0.0157	52.00	45.55	150.10	−3.952	0.345
813	0.0153	49.75	65.21	227.72	−2.499	0.235
823	0.0150	35.50	100.56	828.22	−1.300	0.149
833	0.0146	19.00	271.48	443.50	−0.091	0.054
843	0.0142	3.50	734.69	240.00	+1.182	0.019
853	0.0139	0.75	668.99	125.00	+0.620	0.021

[a] Regression analysis of the data: slope $m = 14.665$, intercept $b = 1.0097$ and correlation coefficient $r = 0.996$.

Examination of the TG curve indicates that Tl(III) glycollate is stable up to 598 K; beyond this temperature it decomposes, without the formation of any stable and isolable intermediate. The decomposition is completed at 863 K. The system decomposes in the temperature range 623–863 K. The loss in weight calculated from the TG curve is 52.25% (theoretical 52.39%). This corresponds to the loss of three glycollate moieties. Thus, the TG and DTG curves show that only one decomposition reaction accompanied by loss in weight takes place. The corresponding DTA curve indicates a large endothermic region with a peak at 833 K. The results therefore indicate that all three glycollate moieties are identically bonded to the Tl(III).

Kinetic parameters

Various kinetic and thermodynamic parameters for the thermal decarboxylation of Tl(III) glycollate were evaluated, employing various computational methods, viz. the Horowitz–Metzger [10], the Freeman–Carroll [11], the Coats–Redfern [12] and the Fuoss [13] methods. The data were then subjected to the method of least squares.

Determination of order of reaction

The order of reaction, n, was determined by applying the Horowitz [10] equation:

$$C_S = (n)^{1/1-n}$$
$$= \frac{W_S - W_f}{W_0 - W_f}$$

where W_S is the weight fraction at T_S, i.e. the DTG peak temperature, and W_0 and W_f are the initial and final weights of the substance. The order of thermal decomposition of Tl(III) glycollate is obtained by comparing the C_S value yielded by the above method with the values given in the Horowitz–Metzger [10] table. The order is calculated to be 1. The Freeman–Carroll method [11], as described below, was also used for the estimation of the order of reaction. This too indicated the order to be unity.

Evaluation of other kinetic and thermodynamic parameters

Other kinetic and thermodynamic parameters, such as energy (E), entropy (S) and free energy (G) of activation and pre-exponential factor (A), were estimated with one or more of the following methods.

(a) Freemand and Carroll method [11]

The Freeman and Carroll treatment, employing the equation

$$\frac{(-E/2.303\mathrm{R})\Delta(1/T)}{\log(W-W_f)} = n + \frac{\Delta\log(\mathrm{d}W/\mathrm{d}t)}{\Delta\log(W-W_f)}$$

where W is the sample weight at temperature T, is shown in Table 1, 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 to a straight line; the intercept on the y axis indicates the order of reaction to be 1. From the slope of the straight line, an activation energy of 279.45 kJ mol^{-1} was obtained (Table 4).

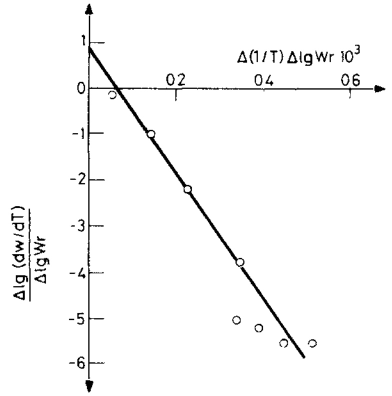


Fig. 2 Freeman and Carroll treatment for tris-thallium(III) glycollate

(b) Coats and Redfern method [12]

The Coats–Redfern relation [12] was also employed in the following form (suitable when $n=1$, as in the present case):

$$\log\frac{-\log(1-\alpha)}{T^2} = \log\frac{A.R}{\Phi.E} - \frac{E}{2.303\,RT}$$

where α = fraction decomposed, A = pre-exponential factor, R = gas constant

and Φ = heating rate in degree s^{-1}. The treatment of the data is shown in Table 2. For the dependence $\log\left[-\log\frac{(1-\alpha)}{T^2}\right]$ vs. T^{-1}, a linear plot (Fig. 3) was obtained. The $E°$ value obtained from the slope of the straight line was 278.9 kJ mol^{-1}. The activation energy E and pre-exponential factor A were calculated from the slope

Table 2 Coats–Redfern treatment for tris-thallium(III) glycollate[a]

Temp., K	$T^{-1} \times 10^3$	$\alpha \times 10^2$	$-\log[-\log(1-\alpha)/T^2]$
773	1.294	5.00	7.066
783	1.277	10.72	6.733
793	1.261	17.50	6.515
803	1.243	25.71	6.336
813	1.230	36.07	6.169
823	1.215	49.29	5.999
833	1.200	72.66	5.726
843	1.186	94.64	5.385
853	1.172	98.93	5.205
863	1.158	100.00	—

[a] Regression analysis of the data: slope $m = 14.795$, intercept $b = -12.087$ and correlation coefficient $r = 0.994$

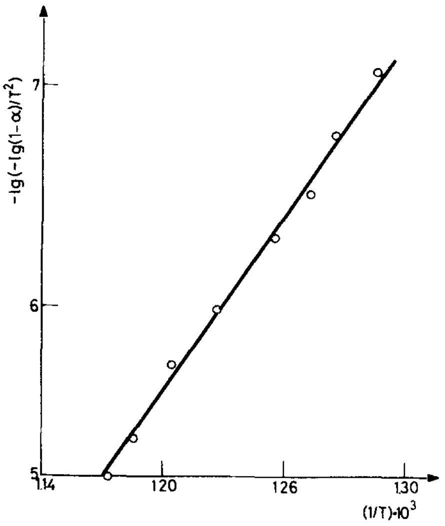


Fig. 3 Coats and Redfern treatment for tris-thallium(III) glycollate

and the intercept on the y axis, respectively. The values so obtained are presented in Table 4.

(c) Horowitz and Metzger method [10]

This method is most commonly used for the estimation of E and A. The equation

$$\log\log\frac{W_0}{W} = \frac{E.\theta}{RT_S^2}$$

where $\theta = T - T_S$, was used for the estimation of E. The treatment of the data by

Table 3 Horowitz–Metzger treatment for tris-thallium(III) glycollate[a]

Temp., K	θ	W_0/W	ln ln W_0/W
773	−60	1.0526	−2.970
783	−50	1.1200	−2.177
793	−40	1.2121	−1.648
803	−30	1.3461	−1.213
813	−20	1.5642	−0.804
823	−10	1.9718	−0.387
833	0	3.6842	+0.265
843	+10	20.0000	+1.097
853	+20	93.0000	+1.512

[a] Regression analysis of the data: slope $m = 18.54$, intercept $b = 2.43$ and correlation coefficient $r = 0.994$

Table 4 Kinetic and thermodynamic parameters obtained by various methods for thermal decarboxylation of tris-thallium(III) glycollate

Computing method[a]	Temp., K	E^b, kJ mol^{-1}	G, kJ mol^{-1}	H,	$-S$, J mol^{-1} K^{-1}	log A s^{-1}
Coats–Redfern	833	281.3	309.5	274.4	42.2	8.17
		(278.9)	(310.0)	(272.0)	(42.8)	(8.10)
Horowitz–Metzger	833	354.9	369.8	348.0	26.2	10.09
		(353.5)	(368.6)	(346.5)	(26.5)	(10.06)
Fuoss	833	279.9	308.4	273.0	42.5	8.13
		(—)	(—)	(—)	(—)	(8.13)
Freeman–Carroll	833	280.8	309.2	273.9	42.4	8.15
		(279.5)	(308.8)	(272.5)	(42.6)	(8.12)

[a] T = inflection temperature; E = energy of activation; G = free energy of activation; H = enthalpy of activation; S = entropy of activation; A = frequency factor.

[b] Values in parentheses are those obtained from the slopes of the straight line plots; other values are from the method of least squares.

this method is shown in Table 3 and the results are plotted in Fig. 4. The values of E and A obtained from the slope and the intercept are given in Table 4. The value of E (353.5 kJ mol^{-1}) is found to be higher as compared with those obtained with the other two methods.

(d) Fuoss method [13]

Fuoss, Salyev and Wilson [13] suggested an expression for the evaluation of E and A for first-order kinetics. These are calculated using the relationships

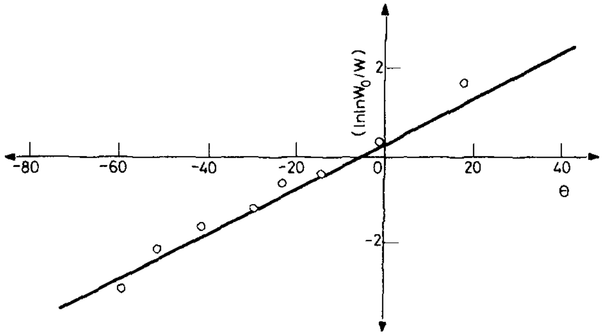


Fig. 4 Horowitz and Metzger treatment for tris-thallium(III) glycollate

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

and

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

In these equations T_i = inflection temperature (K); W_i = weight at the point where the TG curve passes from concave down to concave up; $\left(\frac{\mathrm{d}W}{\mathrm{d}T}\right)_i$ = rate of change in weight at the point of inflection; and a = heating rate. The values of E and A are given in Table 4. The E value (279.89 kJ mol^{-1}) agrees well with those obtained with the Coats–Redfern and Freeman–Carroll methods

If the inter-relationship [21] of A with S is utilized, the latter is calculated via the relation

$$S = (\log A.h/RT_i)R$$

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

As the reaction rate mainly depends on the free energy of activation (G), the activation entropy (S) should decide the magnitude of G according to the relation

$$G = E - T_iS$$

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

$$K_r = A\exp(-E/RT_i)$$

The parameters E, S, G and A calculated with the aforementioned methods and relationships are listed in Table 4.

Regression analysis of the data

In order to obtain precise values of E, the data obtained with the various computational methods were subjected to the method of least squares. The high values of the correlation coefficient (r) obtained from the Coats–Redfern, Horowitz–Metzger and Freeman–Carroll treatments, 0.9937, 0.9935 and 0.9958, respectively, show a very good linearity. The values of E found from the regression analysis in each case agree well with those obtained from the direct slope of the straight line plot, the uncertainty being ± 4.77 kJ mol^{-1}.

From the above results, it is seen that the results of the Coats–Redfern, Freeman–Carroll and Fuoss methods agree very well. However, the kinetic parameters deduced from the Horowitz–Metzger method are somewhat higher than those obtained from the other methods. This is in agreement with our recent observations [22], as well as those of Fong and Chen [23], Sesták et al. [24] and Ozawa [25].

Comparison of the results

Table 4 shows that in general the activation energy (E) for the decarboxylation of Tl(III) glycollate lies around 280 kJ mol^{-1}, with an estimated uncertainty of ± 4.77 kJ mol^{-1}. These values are comparable with the generally accepted values of the activation energy of the decarboxylation reaction [1, 3].

It is interesting to compare the activation energy of thermal decomposition of Tl(III) glycollate with that earlier reported [26] for Tl(III) lactate (263.6 kJ mol^{-1}). The higher value for the former is in accordance with the higher stability of the complex. This indicates that the M—O bond is stronger in Tl(III) glycollate than in the lactate.

It is to be noted further that the rate of thermal decomposition cannot be determined solely by the energy of activation (E), since the frequency factor can vary over a considerable range. It is the free energy of activation (G) which determines the rate of reaction at a given temperature [27]. The higher G, the lower the reaction rate at a given temperature. If the entropy of activation (S) is negative, the activated complex is less probable and the rate is lower [28]. Thus, a large negative entropy of activation and a high free energy of activation mean a slow reaction. The magnitude of the negative entropy of activation in the present case suggests appreciable thermal decarboxylation of Tl(III) glycollate. This is clearly borne out from the shape of the TG curve.

The enthalpy of activation, H, was evaluated from the relationship

$$H = E = RT_i$$

The values of E and H differ by an average of 7.8 kJ mol^{-1}. This small difference could not be assessed experimentally and we can safely say that E and H are equivalent. The error limit in the values of H is ± 2.3 kJ mol^{-1}.

The results presented in Table 4 are within the range usually observed for a first-order reaction [29]. Thus, it can be concluded that the thermal decomposition of Tl(III) glycollate is a first-order reaction.

Conclusion

The above results show that the thermal decomposition of tris-thallium(III) glycollate is a single-step decomposition. This indicates that the three glycollate moieties are identically linked to the central Tl(III). The Freeman and Carroll treatment yields the correct reaction order. The energies of activation obtained with the Coats–Redfern, Freeman–Carroll and Fuoss methods agree excellently. However, the kinetic parameters obtained with the Horowitz–Metzger method are somewhat higher than those obtained with the other three methods. This is in very good accord with our recent observations [22], as well as those of Fong and Chen [23], Šesták et al. [24] and Ozawa [25].

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Zusammenfassung — Die thermische Decarboxylierung von $Tl(GLA)_3$ (GLA = Anion der Glykolsäure) wurde mittels TG, DTG und DTA untersucht. Alle drei Glykolsäureteile treten in einem einzigen Schritt aus. IR Spektren der Liganden und Komplexes weisen auf einen zweizähligen Charakter des Carboxylat-ions und darauf hin, daß das Proton der Hydroxylgruppe während der Komplexbildung nicht ersetzt wird. Die verschiedenen kinetischen und thermodynamischen Parameter der Probe wurden unter Anwendung einiger Berechnungsmethoden bestimmt. Genauere, durch die Methode der kleinsten Fehlerquadrate erhaltene Ergebnisse werden diskutiert.

Резюме — Методом ТГ, ДТГ и ДТА изучено термическое декарбоксилирование соли гликолевой кислоты с трехвалентным таллием. Результаты показали, что выделение всех трех остатков гликолевой кислоты происходит в одну стадию. ИК спектры свободного лиганда и комплекса показали бидентатный характер карбоксилат-иона и отсутствие замещения водородов гидроксильной группы при комплексообразовании. Анализ кривых ТГ, ДТГ и ДТА, проведенный с использованием нескольких расчетных методов, позволил определить различные кинетические и термодинамические параметры. Проведено обсуждение результатов, полученных по методу наименьших квадратов.