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

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Thermal decarboxylation of Tl (GLA), where GLA stands for glycollic acid anion was reported by Khadikar using TG, DTG and DTA techniques. The various kinetic and thermodynamic parameters were evaluated by him from nonisothermal thermogravimetric curve employing different computational methods. Upon re-estimating his data the reaction order and activation energy were found to be 0.67 and 269 kJ/mol respectively, instead of reported reaction order $n = 1$ and activation energy $E = 282$ kJ/mol in the paper under comment.

Methods to find the kinetic and thermodynamic parameters by non-isothermal thermogravimetric data to establish the mechanism of reaction has been under investigation to arrive at a mechanism for the thermal decomposition of transition metal complexes of triphenylphosphine. A computer program [1] has been written in advanced BASIC to compute these parameters by different computational methods Freeman-Carroll [2], Horowitz-Metzger [3], Coats-Redfern [4] and Doyle [5] as modified by Zsakó and Zakó-Zsakó [7] employing minimization and double minimization of standard deviation in the calculations respectively. Khadikar [8] has recently reported the decomposition of tris-thallium(III) glycollate to establish the mechanism and nature of decomposition product. The present paper re-evaluates his data employing different methods [2-7] without making any comments on preparation and characterization of the compound by IR.

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Evaluation of data

Kinetic parameters

Freeman-Carroll method: Freeman-Carroll's final relation is in the form of Eq. (1)

$$\frac{\Delta \ln(\mathrm{d}\alpha/\mathrm{d}t}{\Delta \ln(1-\alpha)} = n - (E/R) \cdot \frac{\Delta(1/T)}{\Delta \ln(1-\alpha)} \tag{1}$$

A plot of $\Delta \ln(\mathrm{d}\alpha/\mathrm{d}t) / \Delta \ln(1-\alpha)$ *vs.* $\Delta(1/T) / \Delta \ln(1-\alpha)$ should result in a straight line with slope $-E/R$ and intercept n which should give the reaction order.

Table 1 Freeman-Carroll treatment for tris-thallium(III) glycollate

Line no.	Temp., K	$(1/T)\cdot 10^3$	W_r	$\log W_r \cdot 10^3$	$(\mathrm{d}W/\mathrm{d}T)\mathrm{d}\cdot 10^3$	$\frac{\Delta \log \mathrm{d}W/\mathrm{d}T}{\Delta \log W_r}$	$\frac{\Delta 1/T \cdot 10^3}{\Delta \log W_r}$
1	773	0.1700	65.50	68.42	20.16	−4.349	0.763
2	783	0.0165	62.50	20.36	25.20	−15.808	0.612
3	793	0.0161	57.75	34.33	94.82	−5.582	0.469
4	803	0.0157	52.00	45.55	150.10	−3.952	0.345
5	813	0.0153	44.45	65.21	227.72	−2.499	0.235
6	823	0.0150	35.50	100.56	828.22	−1.300	0.149
7	833	0.0146	19.00	271.48	443.50	−0.091	0.054
8	843	0.0142	3.50	734.69	240.00	+1.182	0.019
9	853	0.0139	0.75	668.99	125.00	+0.620	0.021

Regression analysis of the data slope $m = 14.665$, intercept $b = 1.0097$ and correlation coefficient $r = 0.996$

A plot of the data from Table 1 (Table 1-4 have been reproduced from [8] for ready reference) is shown in Fig. 1. Activation energy has been calculated from the slope of the straight line and found to be 255 kJ/mol. The intercept of the straight line yields the reaction order which has been found to be 0.67. The following results would be obtained if the line numbers 3, 4, 5, 6, 7 and 9 were subjected to least squares method. Regression analysis yields slope $m = -13.6134$, intercept $a = 0.754$, correlation coefficient $r = 0.999$ and hence $E = 260.43$ kJ/mol and $n = 0.75$. Coats-Redfern's method: Assigning n-type of mechanism, the Eq. (2) is the final version for reaction order, $n = 1$

$$\log\,[-\ln(1-\alpha)/T^2] = \log\,[(A\cdot \mathrm{R})/(\Phi\cdot \mathrm{E})] - E/(2.303\,R\cdot \mathrm{T}) \qquad (2)$$

and for $n \neq 1$ it becomes Eq. (3):

$$\log\,[\{1-(1-\alpha)^{(1-n)}\}/\{(1-n)T^2\}] = \log\,[(A\cdot \mathrm{R})/(\Phi\cdot E)] - E/(2.303\,R\cdot \mathrm{T}) \qquad (3)$$

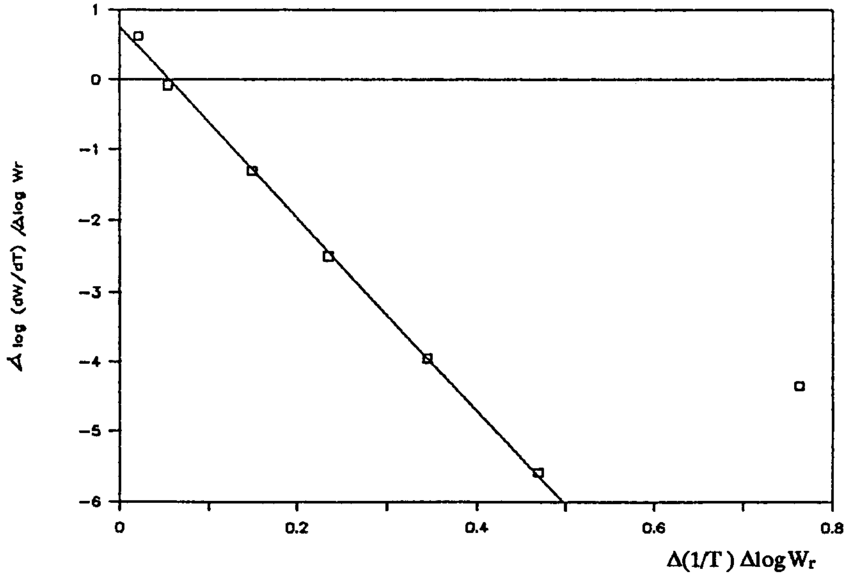

Fig. 1 Freemann-Carroll treatment for tris-thallium(III) glycollate

A plot of either $\log[-\log(1-\alpha)T^2]$ *vs.* $1/T$ for $n=1$ or $\log[\{1-(1-\alpha)^{(1-n)}\}/\{(1-n)T^2\}]$ *vs.* $1/T$ for $n\neq 1$ should give a straight line of slope $-E/R$ for the appropriate value of n.

Coats-Redfern relation (2) and (3) for $n=1$ and $n\neq 1$ respectively were employed for the re-estimation of Khadikar's data and the best linear fit is achieved for $n=0.67$. Plots of the data are depicted in Fig. 2 and from the slope of the straight line, the activation energy was calculated and found to be 245.65 kJ/mol. Subjecting the data to the least squares method yields the following result: regression analysis yields slope $m=-12.7178$, intercept $a=9.4573$, Correlation coefficient $r=0.99$ and hence $E=243.52$ kJ/mol and $n=0.67$, $\log A=7.39$/s Horowitz-Metzger's method: The value of reaction order n is estimated by this method from α_m, the function reacted to T_{m}. If

$1-\alpha_m = 1/e$ then $n = 1$, and the following equation is used to estimate the energy of activation (E)

$$\ln[-\ln(1-\alpha)] = [E/(RT_{\mathrm{m}}^2)]\cdot\Theta \tag{4}$$

where $\Theta = T - T_{\mathrm{m}}$, T_{m} is the temperature at which the rate is maximum, and $f(\alpha)$ is assumed to be $(1-\alpha)^n$. This suggests that a plot of $\ln[-\ln(1-\alpha)]$ *vs.* Θ would be a straight line having a slope E/RT_{m}^2.

Table 2 Coats-Redfern treatment for tris-thallium(III) glycollate

Temp., K	$T^{-1}\cdot 10^3$	$\alpha\cdot 10^2$	$-\log[-\log(1-\alpha)/T^2]$
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	72.56	5.726
843	1.186	94.64	5.385
853	1.172	98.93	5.205
863	1.158	100.00	-

Regression analysisi of the data: slope m = 14.795, intercept b = −12.087 and correlation coefficient r = 0.994

If, however, $1-\alpha_m \neq 1/e$, the Eq. (5) would be used to find reaction order n:

$$1-\alpha_m = (n)^{1/(n-1)} \tag{5}$$

and Eq. (6) would be used to evaluate activation energy E and a plot of the $\ln[\{1-(1-\alpha)^{(1-n)}\}(1-n)]$ *vs.* Θ should give a straight line with slope E/RT_{m}^2.

$$\ln[\{1-(1-\alpha)^{(1-n)}\}/(1-n)] = (E/RT_{\mathrm{m}}^2)\cdot\Theta \tag{6}$$

It is apparent from Table 2 that T_{m} is chosen as 833 K and the corresponding α_m is $72.66\cdot 10^2$

$$1-\alpha_m = 1-0.7266 = 0.2734 \neq 1/e$$

and the reaction order $n = 1$ should not be chosen for the calculation of E and $\log A$. Order of reaction n calculated by utilizing Eq. (5) has been found to be 0.58.

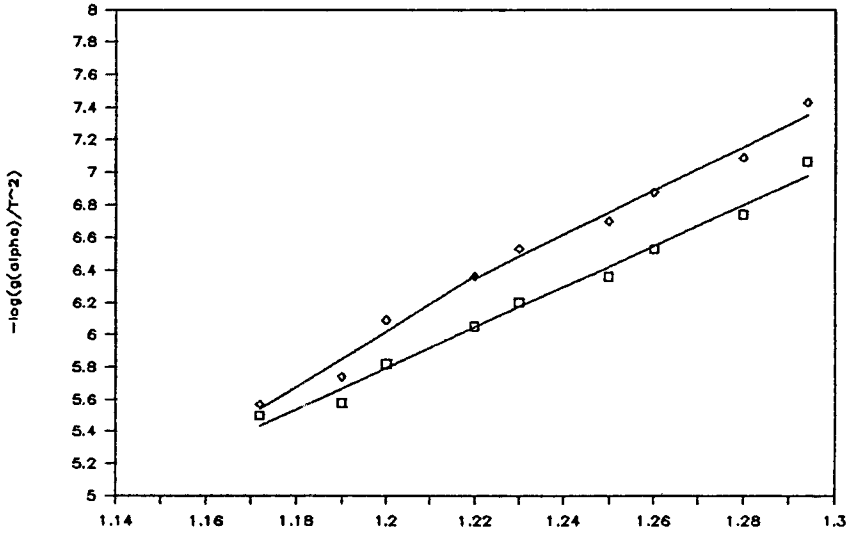

Fig. 2 Coats-Redfern's treatment for tris-thallium(III) glycollate □ - $n=0.67$, ◇ - $n=1$. For $n=1$: $g(\alpha)=-\ln(1-\alpha)$ and for $n\neq1$, $g(\alpha)=[1-(1-\alpha)^{(1-n)}]/(1-n)$

Subjecting the calculated values of $\ln[\{1-(1-\alpha)^{(1-n)}\}(1-n)]$ for reaction order n values equivalent to 0.5, 0.58 and 0.67 and corresponding values of Θ to the least squares method, a high correlation coefficient was achieved for $n = 0.67$. The results are as follows.

Regression analysis: slope $m = 0.047$, intercept $a = 0.0547$, correlation coefficient $r = 0.995$

Kinetic parameters: $E = 270.12$ kJ/mol, $n = 0.67$, $\log A = 14.42$

A plot of $\ln[\{1-(1-\alpha)^{(1-n)}\}(1-n)]$ *vs.* Θ (Fig. 3) gives a straight line with slope 0.046. Calculated value of activation energy from the slope of the straight line is 265.35 kJ/mol.

Regression analysis of the data reported in the footnote in Table 3 [7] is: slope m =18.54, intercept b =2.43 and correlation coefficient r =0.994. However, when the regression analysis was carried out on the data reported in Table 3 the following results were obtained:
slope m =0.054, intercept b =2.43 and correlation coefficient r =0.994

Table 3 Horowitz-Metzger treatment for tris-thallium(III) glycollate

Temp., K	Θ	W_0/W	lnln W_0/W
773	–60	1.0526	–2.970
783	–50	1.1200	–2.117
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

Regression analysis of the data: slope m = 18.54, intercept b = 3.43 and correlation coefficient r = 0.994

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

Computing method	Temp., K	E kJ mol^{-1}	G, kJ mol^{-1}	H, kJ mol^{-1}	$-S$, 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
		(355.5)	(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)

T = inflection temperature; E = energy of activation; G = free energy of activation;
H = enthalpy of activation; S = entropy of activation; A = frequency factor.
Values in parentheses are those obtained from the slopes of the straight line plots; other values are from the method of least squares.

Table 5 Zsakó treatment result

E		*n* = 1		*n* = .67	
kcal/mol	kJ/mol	*δ*	*D*	*δ*	*D*
56	234.304	.11784	.006596	.04914	.00276
58	242.672	.10389	.005636	.04516	.00246
60	251.040	.09105	.004792	.04744	.00251
62	257.410	.07983	.004070	.05522	.00283
64	267.770	.07101	.003520	.06659	.00332
66	276.140	.06556	.003160	.08000	.00388
68	284.512	.06436	.003020	.09468	.00446
70	292.880	.06761	.003098	.11005	.00506
72	301.250	.07475	.003330	.12587	.00564

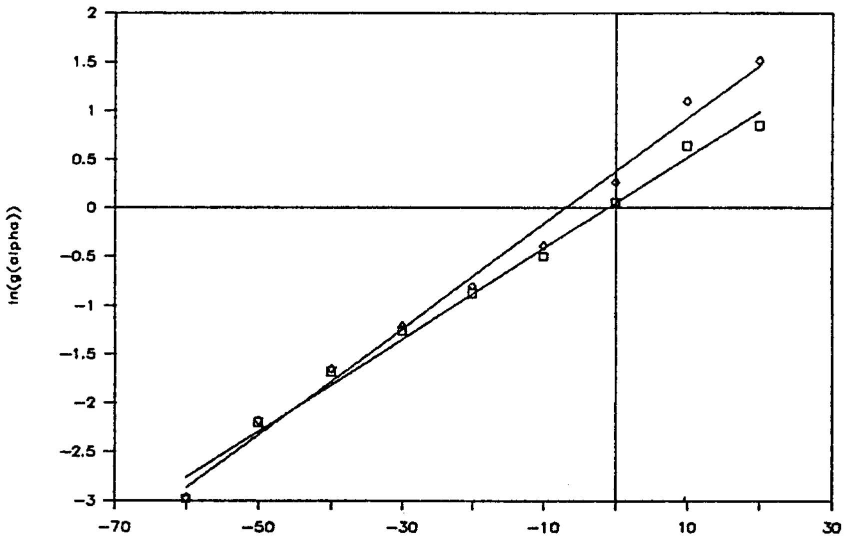

Fig. 3 Horowitz-Metzger treatment tris-thallium(III) glycallate □ - $n=0.67$, ◇ - $n=1$. For $n=1$: $g(\alpha)=-\ln(1-\alpha)$ and for $n\neq 1$, $g(\alpha)=[1-(1-\alpha)^{(1-n)}]/(1-n)$

The high value of the reported slope seems to be either a typographical error which would yield a very high value of activation energy or some sort of omission. Recalculation from the reported data for $n=1$ gives activation energy value of 311.55 kJ/mol instead of 353.5 kJ/mol.

The validity of the re-estimated values has been supported by the Doyle method [5] as modified by Zsakó [6] and Zsakó-Zsakó [7] employing a minimization and a double minimization of the standard deviation respectively.

The results of minimum deviation δ and double minimum deviation D by varying n and E are presented in Table 5. The δ and D values suggest $n = 0.67$ and $E = 242.672$ kJ/mol which are comparable to the values of n and E calculated by Coats-Redfern method.

The values of activation energy are different for different methods. The value of activation energy calculated from Freeman-Carroll method may be taken as reasonable since Chen and Fong [9-11] have tested the three methods [2-4] as well as the one proposed by Achar *et al.* [12] and their conclusion favors the Freeman-Carroll method.

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Zusammenfassung — Unter Anwendung von TG, DTG und DTA beschrieb Khadikar die thermische Decarboxylierung von Tl(GLA) mit GLA = Glykolsäureanion. Mittels verschiedener Rechenmethoden ermittelte er aus der nichtisothermen thermogravimetrischen Kurve verschiedene kinetische und thermodynamische Parameter. In einer Revision seiner Ergebnisse fanden wir anstelle der beschriebenen Reaktionsordnung von 1 und der Aktivierungsenergie von $E = 282$ kJ/mol Werte von 0.67 bzw. 269 kJ/mol.