THERMAL BEHAVIOR AND DECOMPOSITION KINETICS OF A Pr (III) COMPLEX WITH 4, 6-DIHYDROXYAURONE

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ABSTRACT
The use of non-isothermal methods for finding the kinetic parameters (E, Z & ΔS^*) and the mechanism of decomposition of the complex, $[Pr (C_{15}H_9O_4)_3 2H_2O]$ is reported. The complex decomposes in two well defined steps involving random nucleation mechanism. First step involves the dehydration of the complex and the second step involves the loss of the ligand moiety.

KEY WORDS: Thermal behabiour. Complex, 4.6- -Dihyroxyaurone, kinetic parameters etc.

INTRODUCTION
Knowledge of kinetic parameter is one of the keys to determine the reaction mechanisms in solid phases. The present communication deals with the determination of kinetic parameters and the mechanism of decomposition of the reported [1] complex of Pr (III) with 4,6-Dihyroxyaurone.

MATERIALS & METHODS
4,6-Dihydroxy-aurone (ligand) and the complex were prepared by reported method[2]. The aqueous solution of $PrCl_3$ and ethanolic solution of the ligand were mixed in M: L stoichiometric ratio of 1:10. The complex precipitated out readily from the aqueous ethanolic solution. The complex was washed repeatedly with ethanol to remove excess of ligand (the complex itself being insoluble in ethanol) and dried in vacuum over anhydrous calcium chloride. The metal content was estimated gravimetrically as also from the TG Curve. Carbon and hydrogen were estimated by micro-analytical combustion method while I.R.(4000-200) cm^{-1} , d.r.s. (50000-10000) cm^{-1} and thermal studies were done by means of Perkin- Elmer-377 grating I.R spectrophotometer , VSU2P (Carl Zeiss) spectrophotometer and Paulik-Paulik Erdey MOM derivatograph, respectively The sample of the complex $[Pr(C_{15}H_9O_4)_3 2H_2O]$ was heated in paulik-paulik MOM derivatograph (Hungary) [3] for obtaining DTA-DTG and TG curves, when α-Alumina was used as reference inert material. Thermal analysis [4] is defined as a group of techniques in which the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. TGA is a technique in which the mass of the sample is monitored, while DTA monitors the difference in temperature between the sample and a reference material. The kinetic of decomposition steps were investigated by non-isothermal methods [5]. Piloyan-Novikova [6], coats-Redfern [7,8] and Horowitz-Metzger [9,10] methods were employed for finding the kinetic parameters. The graphs of Coats-Redfern, Horowitz-Metzger and α-T (K) were analyzed for the mechanism of decomposition.

RESULT AND DISCUSSION
Thermal analysis is an extremely useful tool in the characterization of material in the research and development field. In differential thermal analysis, temperature changes in the sample are due to reactions caused by phase changes, decomposition, oxidation, reduction or other chemical reactions. In general phase transitions, reduction and decomposition reactions produce endothermic whereas, crystallization and oxidation reaction produce exothermic effects. Fig. I shows the simultaneous DTA, TG and DSC curves of the complex.
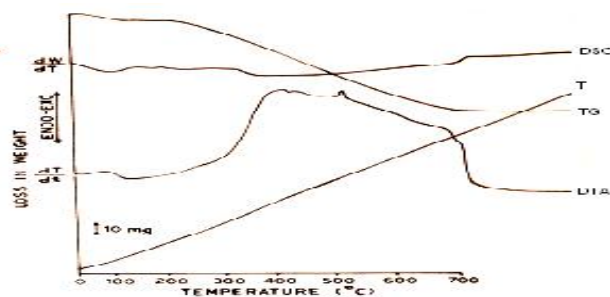

FIGURE 1 Simultaneous DTA, TG and DSC curve of $[Pr(C_{15}H_9O_4)_3 2H_2O]$

The complex decomposes (Fig-I) at 325k and this continues up to 386k which corresponds to the loss of the coordination water molecules. The residual complex starts decomposition further at 473k which continues up to 993k. This corresponds to the loss of the ligand moiety. There is no further loss in weight beyond 993k when a stable oxide Pr_2O_3 as the end product is formed. The proposed decomposition reactions are:
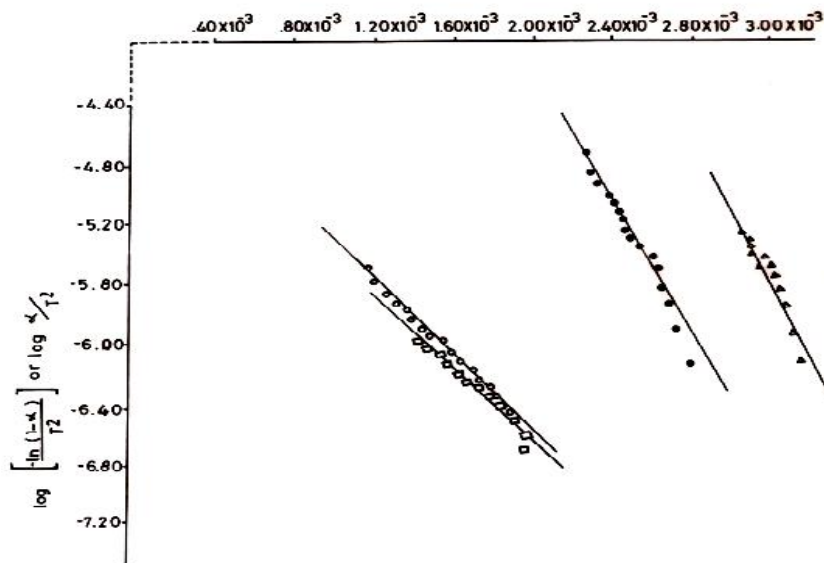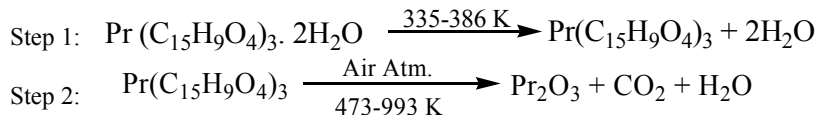
Step 1: $Pr(C_{15}H_9O_4)_3 \cdot 2H_2O \xrightarrow{335-386\ K} Pr(C_{15}H_9O_4)_3 + 2H_2O$

Step 2: $Pr(C_{15}H_9O_4)_3 \xrightarrow[473-993\ K]{Air\ Atm.} Pr_2O_3 + CO_2 + H_2O$

Fig. 2

The fractional weight loss (α) and corresponding $(1-\alpha)^n$ were calculated from TG curve at different temperatures for both the steps of decomposition, where n depends upon the reaction model. The plots: $\log \alpha/T^2$ or $\log [-\ln(1-\alpha)/T^2]$ vs T^{-1} (Fig.2) and $\log [-\ln(1-\alpha)]$ vs. Θ (Fig.3) for Piloyan-Novikova, Coats-Redfern and Horowitz-Metzger respectively are found to be the best-linear fits ($\theta=T-Tm$, where T=Temperature & Tm = peak temperature) Coats-Redfern, Horowitz-Metzger and α-T (K) graph (Fig.4) analyses suggest random nucleation mechanism. Kinetic parameters and mechanism of decomposition are recorded in Table-1.
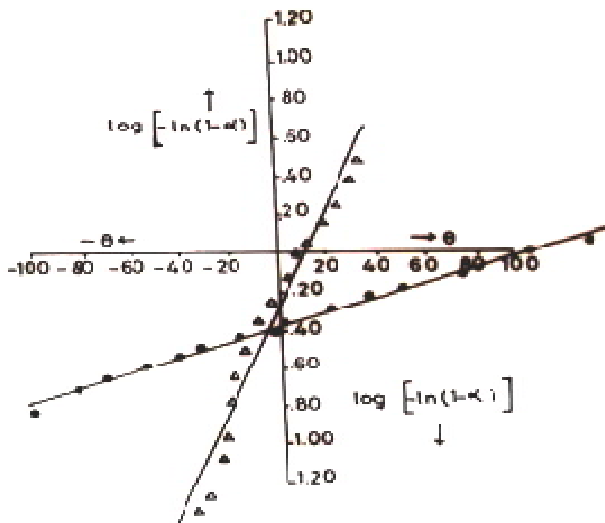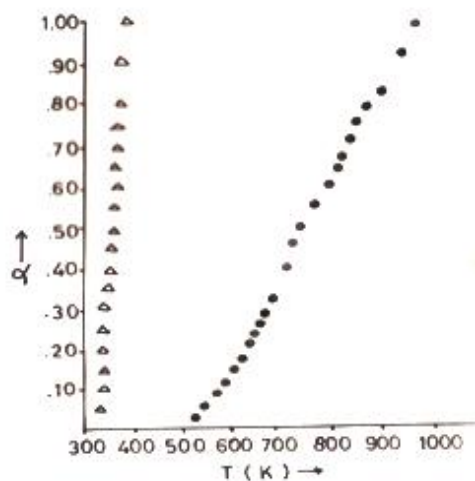

Fig. 3

Fig 4

TABLE- 1

Step	Equation	KJ/ml	Z S^{-1}	ΔS* $JK^{-1}mol$	Model
1st	Piloyan-Novikova	51.6990	8.2318×10^5	-57.7926	-
2nd	Piloyan-Novikova	25.5304	0.0308	-121.9840	-
1st	Coats-Redfern	99.7842	1.2612×10^{-5}	-147.7085	R.N.
2nd	Coats-Redfern	28.7217	0.0676	-119.1472	R.N.
1st	Horowitz-Metzger	32.3778	5.5982×10^{-3}	-126.1981	R.N.
2nd	Horowitz-Metzger	34.2550	1.4502×10^{-3}	-133.022	R.N.

R.N. = Random Nucleation Mechanism.

The graphs (Fig.2 and Fig.3) are analyses for slope, intercept, and energy of activation. The value of intercept and energy of activation (E) are substituted in equation (I) for the value of Z in case of Piloyan-Novikova and Coats-Redfern method while the value of Z in case of Horowitz-Metzger are calculated by using equation (II). The use of equation (III) determines (Δ S*) of activation.

Intercept =   log ZR/βE----------------------I
 Z = E/RTm β exp (E/RTm^2)------------------II
Z = KTm/h exp(ΔS*/R)-----------------------III

Where, R represents the molar gas constant, β the rate of heating (KS^{-1}), K the Boltzmann constant and h the planck's constant.
It is concluded that the complex decomposes into two steps involving random nucleation mechanism.   First decomposing step involves dehydration while the second decomposing step involve the loss of the ligand moiety to form Pr_2O_3 oxide as the end product.
Ligend of figures:-
Fig.1: Simultaneous DTG-DTA-TG curves of the complex
Fig.2: Log α/T^2 VS T^{-1} for Piloyan-Novikova [first step (Δ), second step (□)
Log [-ln (1- α) / T^2 VS T^{-1}] for Coats-Redfern [first step (o), second step (●)]
Fig.3: Horowitz-Metzger Plot-[first step (Δ), second step (●),
Fig.4: α-T (k) graph [first step (Δ), second step (●)

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