



KINETICS AND THERMAL DECOMPOSITION OF Sm (III) COMPLEX WITH EMBELIN (2,5- DIHYDROXY-3-UNDECYL-p-BENZOQUINONE)

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ABSTRACT

The complex $[\text{Sm} (\text{C}_{17}\text{H}_{24}\text{O}_4)_{1.5} (\text{C}_2\text{H}_5\text{OH})_2]_n$ was isolated and characterized by elemental analysis, IR, UV and thermal decomposition studies. The various steps involved in the thermal decomposition of the complex have been analysed by using Piloyan and Novikova, Coats and Redfern, and Horowitz and Metzger equations for evaluating kinetic parameters (E,Z and ΔS^*).

KEY WORDS: Thermal decomposition, Kinetics, Embelin, Piloyan and Novikova, Random Nucleation.

INTRODUCTION

Embelin is a biologically active benzoquinone derivative [1-3]. Embelia ribes found to have antiproliferative properties, wound healing activity, antibacterial, antitumour, anti-inflammatory and analgesic activity [4-5]. Purified embelin also shows antifertility, antioestrogenic and anthelmintic activities. Embelin cream (E 0.05%) is sold as cheap global discount cancer drug. Some complexes of embelin are reported [6]. Lanthanide (III) complexes have biological [7] and light emitting [8] applications. There is limited reference in literature regarding differential thermal analysis and thermogravimetric studies of such polymeric complexes. Keeping in view the importance of embelin. It was thought interesting to study the thermogravimetric analysis and the kinetics of thermal decomposition of the Sm(III) complex.

MATERIALS AND METHODS

The biologically active compound embelin (2,5-dihydroxy-3-undecyl-p-benzoquinone) was isolated from embelia ribe seeds [9]. Its complex with Sm (III) was prepared by the reported method [6]. The complex prepared was stored under vacuum over anhydrous calcium chloride. The metal content was estimated gravimetrically as also from the TG curve. C and H were estimated by using micro-analytical combustion method. The IR spectra of the ligand and the complex were recorded using KBr pellets recorded on Perkin Elmer-377 grating IR spectrophotometer, while the electron spectrum of the complex was recorded as diffuse reflectance spectrum in the 50,000-10,000 cm^{-1} region. The simultaneous TG and DTA curves of the complex were obtained on Paulik-Paulik MOM derivatograph (Hungary) at the heating rate of 10° per minute in static air atmosphere when α -Alumina was used as a reference inert material. The powdered sample was loosely and uniformly packed in a cylindrical heat resistant ceramic crucible. The fractional weight loss (α) at different temperatures

was calculated from TG graph, during various steps of decomposition. The kinetic of decomposition steps were investigated by non isothermal methods [10]. For obtaining the Kinetic parameters and the reaction model, the thermo gravimetric data was analyzed by making use of appropriate equations commonly used in non-isothermal kinetic studies of decomposition reactions. The model giving best linear fit for different equations was considered.

RESULTS & DISCUSSION

The comparison of the IR spectra of the ligand and the complex ascertained the coordination sites of the ligand and the nature of the complex [6,9-11]. 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. The thermal decomposition of the complex occurs in three distinct steps as obtained in the TG and the corresponding peaks of the DTA curves (Fig.1). The decomposition starting at 333K and continuing upto 493K when a horizontal portion of the curve is obtained. The weight remaining at this stage corresponding to $[\text{Sm} (\text{C}_{17}\text{H}_{24}\text{O}_4)]_{1.5}]_n$ which indicates the loss of the two ethanol molecules. A further regular decomposition starting at 493K and extending up to 701K in corresponding to loss of the side chain of the ligand. The weight remaining at this stage corresponding to $[\text{Sm} (\text{C}_6\text{H}_1\text{O}_4)_{1.5}]_n$. At 701K, a further gradual loss in weight starts, continuing upto 893K and corresponding to the loss of the remainder of the benzoquinone moiety. At 893K, another horizontal portion is obtained. The weight at this stage corresponding to Sm_2O_3 which remained stable during subsequent heating. The proposed decomposition reactions are:

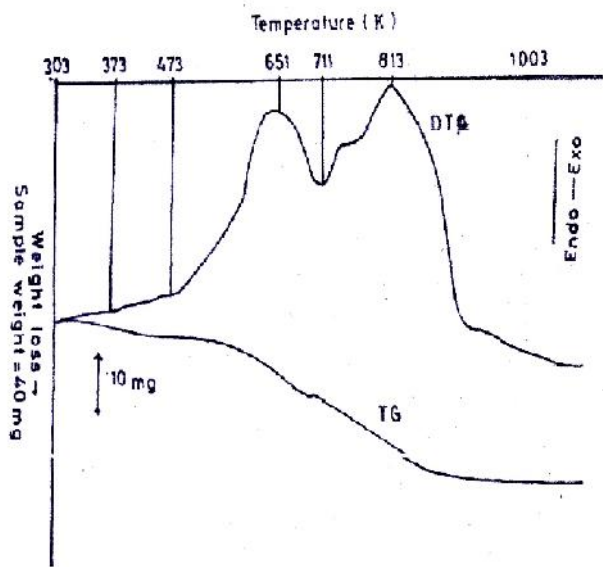
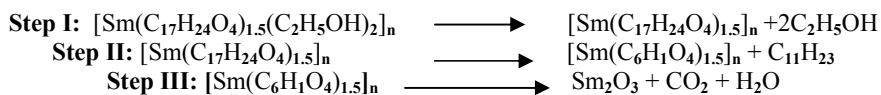


Fig. 1 Simultaneous TG-DTA curves, Sample wt = 40 mg

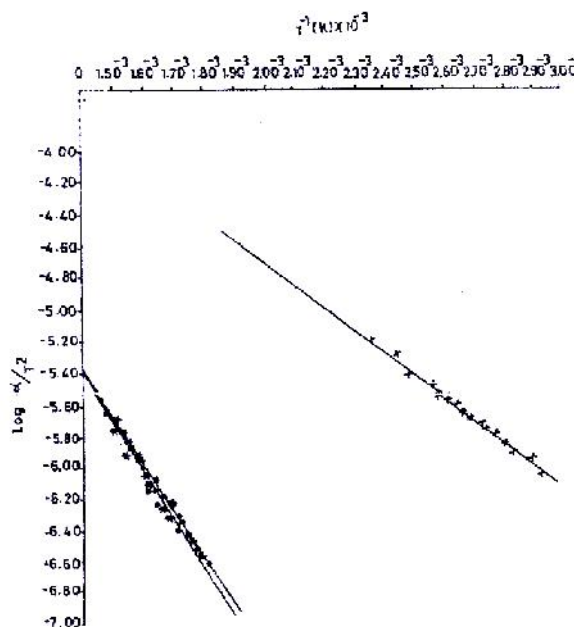


Fig. 2 Piloyan-Novikova Plots : First step (x) Second step (*), Third step (•)

Kinetic of the decomposition

Non isothermal kinetics of three steps of decomposition has been studied. From the values of α , corresponding $(1-\alpha)^n$ values were calculated where n depends upon the reaction model. The corresponding value of $g(\alpha) = d\alpha \int_0^\alpha f(\alpha)$ were calculated for equations: Piloyan and Novikova [12]; Coats and Redfern [13-14], and Horowitz and Metzger [15-16] with different values of n. For Piloyan and Novikova, plot of $\log(\alpha/T^2)$ vs. $1/T$; for Coats and Redfern, plot of $\log[-\ln(1-\alpha)T^2]$

vs. $1/T$, and for Horowitz and Metzger equation, plot of $\log[-\ln(1-\alpha)]$ vs. θ , were found to be best linear fits ($\theta = T - T_m$; where T=Temperature and T_m =peak temperature). The plots obtained are shown in Fig.(2-4). The model which corresponds to the best linear fit has been used to give the probable mechanism of decomposition. The value of slope, intercept, and the energy of activation (E) were calculated from the graphs. (Fig.3-5).

TABLE 1. Non-isothermal kinetic studies of the complex

Step	Equation	E KJmol ⁻¹	Z S ⁻¹	ΔS* JK ⁻¹ mol ⁻¹	Model
First	Piloyan and Novikova	25.53	5.61	-101.31	--
	Coats and Redfer	25.19	5.16	-102.77	R.N.
	Horowitz and Metzger	31.82	0.94	-107.73	R.N.
Second	Piloyan and Novikova	54.37	39.58	-95.86	--
	Coats and Redfern	7.180	185.43	-90.28	R.N.
	Horowitz and Metzger	71.24	0.008	-130.79	R.N.
Third	Piloyan and Novikova	59.91	102.87	-93.25	--
	Coats and Redfern	78.98	308.74	-89.28	R.N.
	Horowitz and Metzger	98.87	0.003	-130.81	R.N.

R.N. Random Nucleation Mechanism

The values of the intercept and the energy of activation are substituted in the following equation (1) for evaluating the values of Z in case of the Piloyan-Novikova and Coats- Redfern methods.

$$\text{Intercept} = \frac{ZR}{BE}$$

The value of Z in case of Horowitz and Metzger method were calculated by using the following equation. $Z = E/RT_m \beta \exp(E/RT_m^2)$.

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And the value of entropy of activation (ΔS^*) was obtained from the equation.

$$Z = K T m / h \exp (\Delta S^* / R)$$

Where, R represents molar gas constant, β the rate of heating ($K S^{-1}$), K the Boltzmann constant and h the plank's constant.

The value of kinetic parameters and the mechanism for which the best linear fit was obtained by applying the above equations are recorded in table-I.

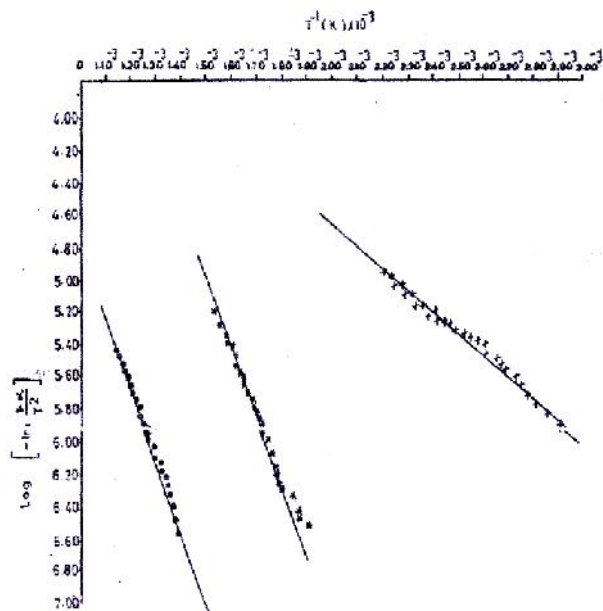


Fig. 3 Coats-Redfern Plots : First step (x) Second step (*), Third step (•)

It is obvious that the values of various kinetic parameters obtained from the different equations are in good agreement. The complex of embelin with Sm (III) has a regular decomposition pattern with loss of ethanol as the first step, loss of the side chain of the ligand as the second step and the third step involving the loss of the complete ligand moiety giving Sm_2O_3 as the end product. The entire three decomposition steps involve random nucleation mechanism [17].

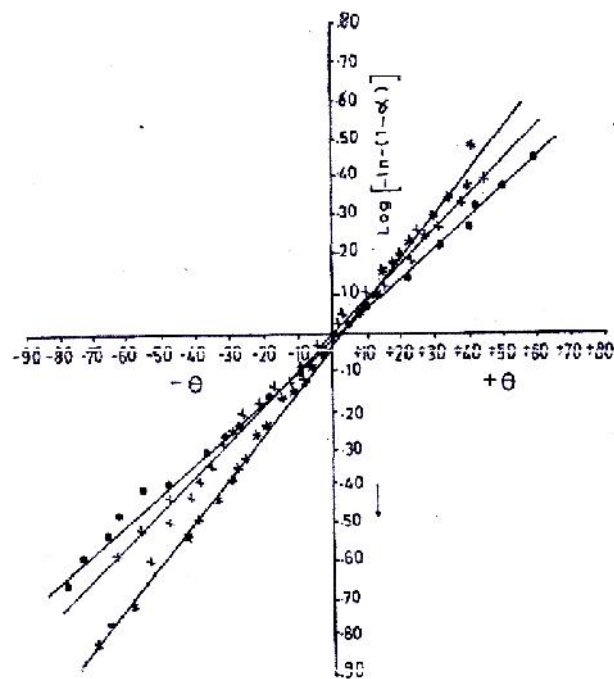


Fig. 4 Horwitz-Metzger Plots : First step (x) Second step (*), Third step (•)

REFERENCES

- [1]. S Pranjpe and G K Ghokale, *J. Mol. Cat.*, 198 (2003) 175
- [2]. T Tang and F Wu, *Tianran Chanwu Yanjiu Yu Kaifa*, 16 (2004)129
- [3]. X Huang and X Huang, *Fajiao Gongye SY*, 32 (2006) 108
- [4]. Beena Jay and S. Lakshmi, *The Open Process Chemistry Journal*, 3 (2010)17-22.
- [5]. M Chitra, Devi SCS and E Sukumar, *Fitoterapia*, 74 (2003) 401-403.
- [6]. M L Dhar and Onkar Singh, *Inorganic Chimica Acta*, 117 (1986) 187-185
- [7]. T Premkumar and S Govindarajan, *J. Microbiol. Biotechnol*, 2006, 22, 1105.
- [8]. D Vyprachticky and V Gimrova, *Macromolecules*, 2002, 35, 3463.
- [9]. Ch Rao Bheemaskara, V. Venkteswarlu, *Indian J. Pharama*, 27(1962)263.
- [10]. Sehgal And D Fatu, "Introdustion to Non- Isothermal Kinetics, academic ed, Bacharest, 1983.
- [11]. A Finch, P N Gates, K Radcliffe, N F Dischson and F E Bentley, 'Chemical application of for infra red Spectroscopy (academic Press, New York) 1970.
- [12]. G O Piloyan, I D Pyabchikov and I S Novikova *Nature* (London) 212 (1966)1229.
- [13]. A W Coats and J P Redfern, *Nature* (London) 68 (1964), 201.
- [14]. R Ebrahimi-Kahrizangi and M H Abassi, *Trans Non ferrous Met. Soc. China* 18 (2008), 217-221.
- [15]. H Horwitz and G Metzger, *Anal Chem.*35 (1964), 1464.
- [16]. M A Ashok and B N Achar, *Bull.Mat. Sci* 3192008),29-35.
- [17]. K L Manpal, *Z Phys. Chem.* 187(1940), 43 and 235.