KINETICS OF THERMAL DEHYDRATION OF La(III) AND Yb(III) COMPLEXES WITH ORTHO-VANILLIN OXIME

*M. L. Dhar** and O. Singh*

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JAMMU, JAMMU-180001, INDIA

The analysis of dehydration of the complexes, [La(C8H8NO3)3.2H2O] and [Yb(C8H8NO3)3.3H2O] for the evaluation of kinetic parameters (Z, E & ΔS^*) and mechanism of dehydration by non-isothermal methods are reported. The complexes decompose in three well defined steps involving random nucleation mechanism. First two steps involving the dehydration and the third step the loss of the ligand moiety. The intermediates formed during decomposition were found to be unstable for carrying out any significant studies.

The complexes have been already characterized [1]. The present investigation deal with the mechanism of dehydration of complexes and the evaluation of kinetic parameters of the complexes.

Experimental

Paulik-Paulik MOM derivatograph [2] was employed for recording of simultaneous DTA, DTG and TG curves of the complexes. The samples were heated at the rate of 10 deg/min in a cylindrical heat resistant ceramic crucible, α-alumina was used as the reference material.

Non-isothermal methods: Piloyan-Novikova [3], Coats-Redfern [4] and Horowitz-Metzger [5] were employed to analyze the thermogravimetric data and for establishing the mechanism of dehydration. The graph α-T(K) was also analyzed to support the mechanism of dehydration.

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* To whom correspondence should be addressed

Results and discussion

[La(C$_8$H$_8$NO$_3$).2H$_2$O] complex (Fig. 1) starts decomposing at 373 K and this step continues upto 418 K when a rest appears in the curve. The weight remaining at this stage corresponds to [La(C$_8$H$_8$NO$_3$)·H$_2$O] indicating the loss of one coordinated water molecule. The complex further decomposes at 418 K and this process continues upto 553 K when again a small distinguishable rest is observed. This corresponds to the complete dehydration of the complex. The next decomposition steps continues upto 893 K corresponding to the loss of the ligand moiety. Beyond this temperature there is no weight loss as the stable oxide La$_2$O$_3$ is formed.
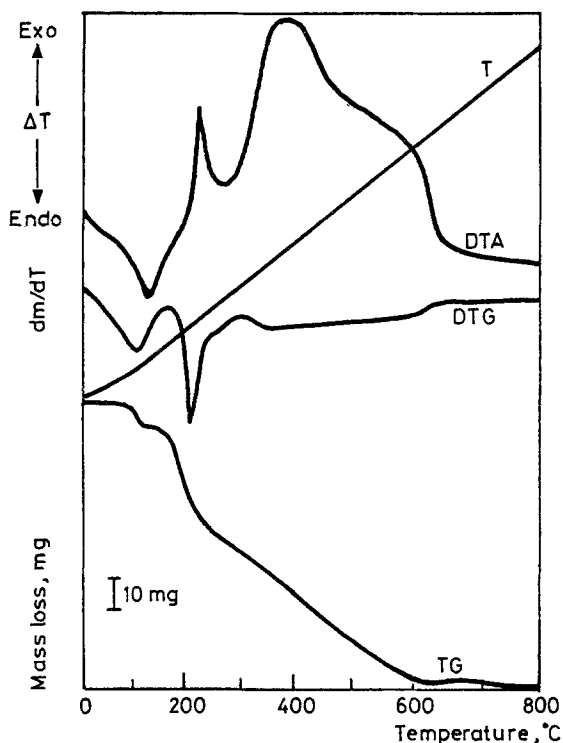

Fig. 1 Simultaneous DTG-DTA-TG curves of [La(C$_8$H$_8$NO$_3$)·2H$_2$O] complex

Similarly, [Yb(C$_8$H$_8$NO$_3$)$_3$.3H$_2$O] complex (Fig. 2) starts decomposing from 333 K to 433 K corresponding to the loss of one coordinated water molecule. Further decomposition from 480 K to 595 K corresponds to the loss of the remaining two coordinated water molecules. There is further loss
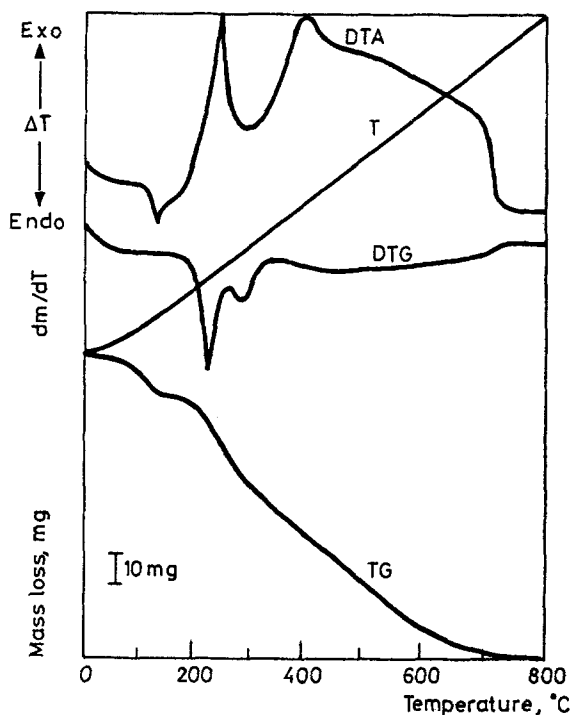
Fig. 2 Simultaneous DTG-DTA-TG curves of [Yb(C₃H₈NO₃)·3H₂O] complex

in weight upto 994 K due to the loss of the ligand moiety. Beyond this temperature there is no further loss in weight as the stable oxide Yb_2O_3 is formed.

Table 1 shows the value of kinetic parameters and the mechanism of decomposition obtained by using non-isothermal kinetics methods of decomposition.

The fractional weight loss (α) and corresponding $(1-\alpha)^n$ are calculated from TG curves at different temperatures during first two steps of decomposition, where n depends upon the reaction model. The plots of $\lg \dfrac{\alpha}{T^2}$ vs.

$\dfrac{1}{T}$ (Fig. 3), $\lg \left[\dfrac{-\ln(1-\alpha)}{T^2} \right]$ vs. $\dfrac{1}{T}$ (Fig. 4) and $\lg [-\ln(1-\alpha)]$ vs. Θ (Fig. 5) plotted for Piloyan-Novikova, Coats-Redfern and Horowitz-Metzger respectively are found to be the best linear fits, where $\Theta = T-Tm$, Tm = peak temperature. Coats-Redfern and Horowitz-Metzger graphs supported by α-

Table 1

Complex	Step	Equation	E, kJ/mol	Z, S^{-1}	ΔS^*, $JK^{-1}mol^{-1}$	Model
$[La(C_8H_8NO_3)_3\cdot 2H_2O]$	1st	Piloyan-Novikova	98.9301	5.0980×10^{-3}	-18.3205	-
	Second	Piloyan-Novikova	55.0499	1.2373×10^{9}	-32.5920	-
$[Yb(C_8H_8NO_3)_3\cdot 3H_2O]$	1st	Piloyan-Novikova	40.0363	4.3107×10^{2}	-85.3375	-
	Second	Piloyan-Novikova	78.9846	7.2376×10^{4}	-90.7979	-
$[La(C_8H_8NO_3)_3\cdot 2H_2O]$	1st	Coats-Redfern	88.0798	0.4976×10^{10}	-26.7221	R.N.
	Second	Coats-Redfern	84.2503	1.9845×10^{6}	-55.8230	R.N.
$[Yb(C_8H_8NO_3)_3\cdot 3H_2O]$	1st	Coats-Redfern	55.8470	8.8940×10^{4}	-66.1610	R.N.
	Second	Coats-Redfern	86.1651	4.7577×10^{5}	-61.2938	R.N.
$[La(C_8H_8NO_3)_3\cdot 2H_2O]$	1st	Horowitz-Metzger	117.0933	7.4233	-100.106	R.N.
	Second	Horowitz-Metzger	72.8949	6.5042×10^{-3}	-126.3715	R.N.
$[Yb(C_8H_8NO_3)_3\cdot 3H_2O]$	1st	Horowitz-Metzger	57.6029	8.9309×10^{-3}	-124.2774	R.N.
	Second	Horowitz-Metzger	99.7598	7.6024×10^{-3}	-126.1154	R.N.

R.N. = Random Nucleation Mechanism

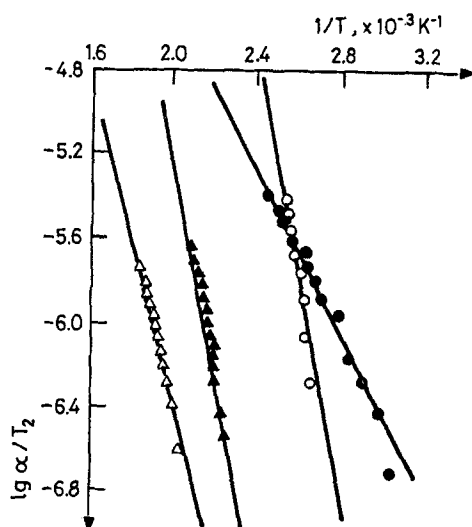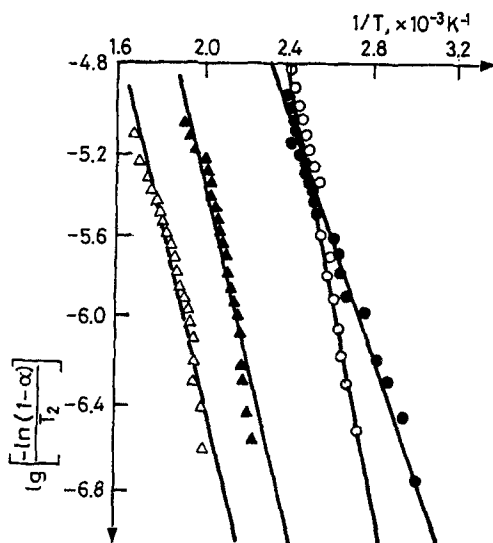**Fig. 3** Piloyan-Novikova plots: La(III)complex [1st step (o) 2nd step (▲)], Yb(III)complex [1st step (●), 2nd step (Δ)

Fig. 4 Coats-Redfern plots: La(III)complex [1st step (o) 2nd step (▲)], Yb(III)complex [1st step (●), 2nd step (Δ)

$T(K)$ graph (Fig. 6) suggest random nucleation mechanism [6]. The α-$T(K)$ curves constructed on the basis of TG data for the first two steps of decom-
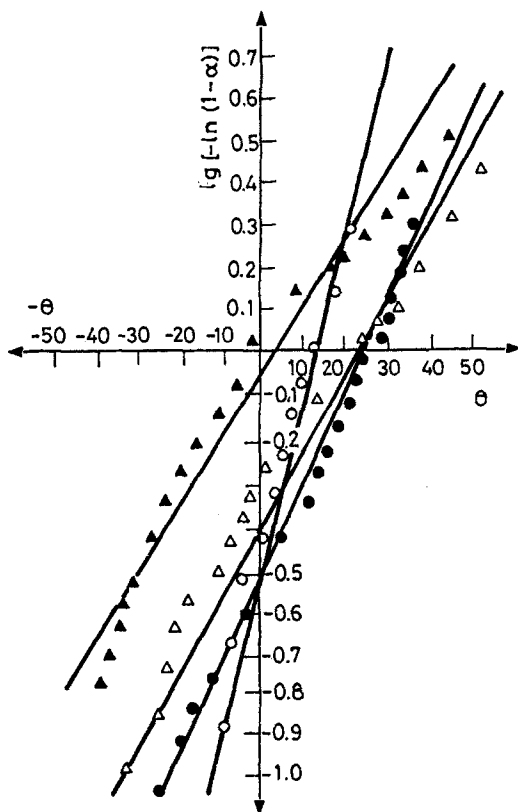
Fig. 5 Horowitz-Metzger plots: La(III)complex [1st step (o) 2nd step (▲)], Yb(III)complex [1st step (●), 2nd step (Δ)

position of both the complexes are of the same pattern. The curves begin with an acceleratory period without any apparent induction period, thus indicated that no surface nucleation or branching occurs before the start of these steps [7].

Slope, intercept and energy of activation (E) obtained from graphs (Figs 3-5) were substituted in Eq. (1) to get the values of Z in case of Piloyan-Novikova and Coats-Redfern while the values of Z in case of Horowitz-Metzger were calculated by using Eq. (2). The entropies (ΔS^*) of activation were calculated by using Eq. (3).

$$\text{Intercept} = lg\frac{ZR}{\beta E} \qquad (1)$$

$$Z = \frac{E}{RTm} \, \beta \, \exp\left(\frac{E}{RTm^2}\right) \qquad (2)$$

$$Z = \frac{KTm}{h} \, \exp\left(\frac{\Delta S^*}{R}\right) \qquad (3)$$

Where, R represents the molar gas constant, β the rate of heating (KS^{-1}), K the Boltzman constant and h the Planck's constant.
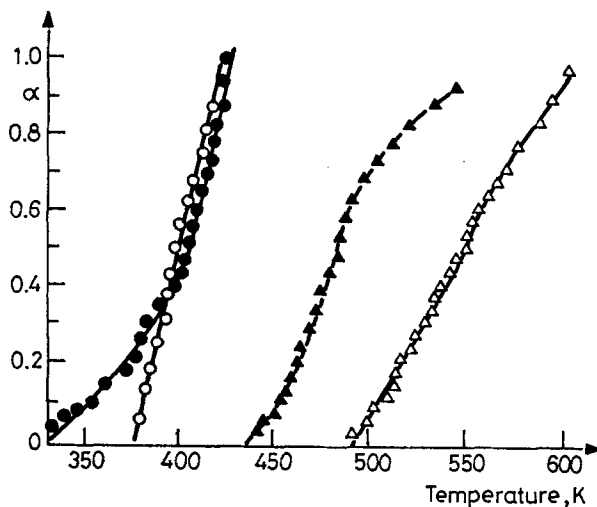

Fig. 6 α vs. T (K) graph: La(III)complex [1st step (o) 2nd step (▲)], Yb(III)complex [1st step (●), 2nd step (Δ)

The data indicates that both the complexes undergo complete dehydration in the first two steps of decomposition. The third step involves the loss of the ligand moiety with the formation of the stable oxides La_2O_3 and Yb_2O_3 as the end product. The dehydration involves the random nucleation mechanism.

References

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Zusammenfassung — Zwecks Ermittlung der kinetischen Parameter (Z, E und S^{*}) und des Mechanismus der Dehydratierung durch nichtisotherme Verfahren wird die Analyse der Dehydratierung der Komplexe [La($C_8H_8NO_3$)$_3 \cdot 2H_2O$] und [Yb($C_8H_8NO_3$)$_3 \cdot 3H_2O$] beschrieben. Die Komplexe zersetzen sich in drei gut definierten Schritten mit Random-Keimbildungsmechanismus. Die ersten zwei Schritte beinhalten die Dehydratierung, der dritte Schritt den Verlust der Liganden. Die während der Zersetzung entstandenen Zwischenprodukte erwiesen sich für jegliche signifikante Untersuchung als zu unstabil.