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Note

THERMAL STUDIES ON TRIS(2-HYDROXY-1,4-NAPHTHOQUINONATO) Eu(III), Gd(III) and Tb(III)

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A large amount of work has been done on hydroxynaphthoquinones by Sawhney and coworkers [1–10]. This note highlights the pyrolysis and kinetic studies on tris(2-hydroxynaphthoquinonato) Eu(III), Gd(III) and Tb(III).

EXPERIMENTAL

All the chemicals used were of analytical grade. Metal complexes were isolated with the addition of the metal to the sodium salt of 2-hydroxy-1,4-naphthoquinone with constant stirring until the metal content slightly exceeded the 1 : 3 stoichiometric ratio of the complex. The precipitate was filtered, washed with distilled water and dried at 35–40 °C. Elemental analysis gave the formula $(C_{10}H_5O_3)_3 \cdot M$, where M = Eu, Gd and Tb. A Stanton Redcroft thermal analyser STA Model 781 was employed to record the thermograms of the complexes (10 °C min^{-1}).

RESULTS AND DISCUSSION

The metal complexes, when taken through a wide range of temperature, produced fragments which gave an indication of the course of decomposition and the nature of the intermediate formed. Two sigmoid shapes were obtained in each of the pyrolysis curves of the metal complexes. The thermogram of tris(2-hydroxy-1,4-naphthoquinonato) Eu(III) pointed to the onset of decomposition of the complex at 55 °C continuing to 260 °C, after which a plateau from 260 to 404 °C with the formation of the intermediate species, $Eu(C_{10}H_5O_3)$, was obtained. Between 404 and 504 °C all the organic matter was lost forming Eu_2O_3 which remained constant after 650 °C. The gadolinium complex $[Gd(C_{10}H_5O_3)_3]$ was stable up to 62 °C. Between 62

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and 275°C 12/5 $C_{10}H_5O_3$ was lost forming [Gd(3/5 $C_{10}H_5O_3$)] indicated by a plateau (275–413°C). The remaining organic matter was lost from 413 to 482°C, forming Gd_2O_3. The terbium complex [Tb($C_{10}H_5O_3$)$_3$] was stable up to 68°C; its organic part (5/4 $C_{10}H_5O_3$) was lost between 68 and 194°C. A plateau (194–378°C) indicated [Tb(7/4 $C_{10}H_5O_3$)]. Further organic matter was lost from 378 to 482°C. A plateau (> 482°C) indicated Tb_2O_3.

The endotherms are shown below

Complex	Endotherms (°C)
Eu	267.25, 404
Gd	275, 642
Tb	194, 482

Corresponding to the sigmoid shapes on the TG trace, the dips on the DTG trace were also observed.

Each of the sigmoids shapes were analysed for the kinetics of the non-isothermal decomposition of the complexes, employing the non-slope dependent procedure of Dave and Chopra [11].

TABLE 1

Pyrolysis data on tris(2-hydroxy-1,4-naphthoquinonato)M(III) (M = Eu, Gd, Tb)

Stable phases (temp. range) (°C)	Loss	% Loss		% Metal oxide	
		Calc.	Found	Calc.	Found
Eu($C_{10}H_5O_3$)$_3$ (55)					
Eu($C_{10}H_5O_3$) (404–504)	2 $C_{10}H_5O_3$	51.03	50.59		
Eu_2O_3 (650)	$C_{10}H_5O_3$ + 2 $C_{10}H_5O_3$	76.55	73.02	26.99	27.96
Gd($C_{10}H_5O_3$) (62)					
Gd(3/5 $C_{10}H_5O_3$) (413–482)	12/5 $C_{10}H_5O_3$	62.40	61.50		
Gd_2O_3 (642)	3/5 $C_{10}H_5O_3$ + 12/5 $C_{10}H_5O_3$	77.54	76.02	26.66	25.67
Tb($C_{10}H_5O_3$)$_3$ (68)					
Tb(7/4 $C_{10}H_5O_3$) (378–482)	5/4 $C_{10}H_5O_3$	62.58	61.62		
Tb_2O_3 (575)	7/4 $C_{10}H_5O_3$ + 5/4 $C_{10}H_5O_3$	76.66	74.68	31.90	31.28

TABLE 2

Kinetic data on non-isothermal decomposition of metal complexes of 2-hydroxy-1,4-naphthoquinone

Reaction	DCM (2) [a]		DCM (3) [b]			BDM (4) [c]		
	E	n	E	n	log Z	E	n	log Z
$Eu(C_{10}H_5O_3)_3 \xrightarrow{55-260\,^\circ C}$								
$Eu(C_{10}H_5O_3) + 2\,C_{10}H_5O_3\uparrow$	5.25	0.78	6.1	1	0.79	4.97	1	1.12
$Eu(C_{10}H_5O_3) \xrightarrow{404-504\,^\circ C} Eu_2O_3 + d.p.\uparrow$	4.79	1.00	4.2	1	1.19	4.19	1	1.14
$Gd(C_{10}H_5O_3)_3 \xrightarrow{62-275\,^\circ C}$								
$Gd(3/5\,C_{10}H_5O_3) + 12/5\,C_{10}H_5O_3\uparrow$	5.99	0.65	5.3	1	0.99	5.57	1	0.89
$Gd(3/5\,C_{10}H_5O_3) \xrightarrow{413-482\,^\circ C}$								
$Gd_2O_3 + 3/5\,C_{10}H_5O_3\uparrow$	5.67	0.68	4.7	1	0.98	5.06	1	0.82
$Tb(C_{10}H_5O_3)_3 \xrightarrow{68-194\,^\circ C}$								
$Tb(7/4\,C_{10}H_5O_3) + 5/4\,C_{10}H_5O_3\uparrow$	5.16	0.78	5.3	1	1.24	4.38	1	1.10
$Tb(7/4\,C_{10}H_5O_3) \xrightarrow{378-482\,^\circ C}$								
$Tb_2O_3 + 7/4\,C_{10}H_5O_3\uparrow$	4.19	0.70	4.7	1	1.15	5.25	1	1.25

[a] DCM (2), Dave and Chopra method [11]. [b] DCM (3), Dave and Chopra method [11]. [c] BDM (4), Borchardt and Daniels method [13].

The accompanying reactions, (1)–(6), resembling the reaction of the type, A(s) → B(s) + C(g), obtained for the kinetics of the solid state reaction by Freemann and Carroll [12],

$$Eu(C_{10}H_5O_3)_3 \xrightarrow{55-260\,^\circ C} Eu(C_{10}H_5O_3) + 2\,C_{10}H_5O_3\uparrow \quad (1)$$

$$Eu(C_{10}H_5O_3) \xrightarrow{404-504\,^\circ C} Eu_2O_3 + d.p.\uparrow \quad (2)$$

$$Gd(C_{10}H_5O_3)_3 \xrightarrow{62-275\,^\circ C} Gd(3/5\,C_{10}H_5O_3) + 12/5\,C_{10}H_5O_3\uparrow \quad (3)$$

$$Gd(3/5\,C_{10}H_5O_3) \xrightarrow{413-482\,^\circ C} Gd_2O_3 + 3/5\,C_{10}H_5O_3\uparrow \quad (4)$$

$$Tb(C_{10}H_5O_3)_3 \xrightarrow{68-194\,^\circ C} Tb(7/4\,C_{10}H_5O_3) + 5/4\,C_{10}H_5O_3\uparrow \quad (5)$$

$$Tb(7/4\,C_{10}H_5O_3) \xrightarrow{378-482\,^\circ C} Tb_2O_3 + 7/4\,C_{10}H_5O_3\uparrow \quad (6)$$

follow first-order kinetics; further the reactions are slow since log Z has an abnormally low value. Borchardt and Daniels' equation [13] was also employed for such a study. The analysis showed that the kinetic data obtained by the above methods were in agreement. In Table 1 and 2 the details of the pyrolysis and the kinetic data are presented.

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