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Note

EVALUATION OF THE KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF METAL CHELATES OF LAPACHOL WITH YTTRIUM(III), INDIUM(III), SAMARIUM(III), GADOLINIUM(III) AND DYSPROSIUM(III) FROM THERMOGRAVIMETRIC CURVES

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In recent years, lapachol has received attention as a chelating agent [1—3]. The literature reveals that the pyrolytic decomposition of the metal—lapachol chelates has not been probed kinetically. Investigations, based on the work of Dave and Chopra [4] and Freeman and Carroll [5], were therefore planned and initiated for the estimation of the kinetic parameters for the pyrolysis of metal chelates of lapachol with Y(III), In(III), Sm(III), Gd(III) and Dy(III).

EXPERIMENTAL

All chemicals used were either of B.D.H. or Aldrich Analar. For isolation of metal chelates in the solid state, lapachol solution prepared in one equivalent sodium hydroxide was added slowly with constant stirring to the metal ion solution. The coloured precipitate was digested for 0.5 h over a water bath and filtered on a sintered crucible, washed with ice-cooled water and dried at 45°C. For C and H analysis, Therelec was employed. The experimental percentages of C and H in different metal—lapachol chelates were in agreement with theoretical values (Table 1).

For TG tracings, the Cahn automatic electrobalance, equipped with Fischer programmer-360, Fischer furnace 260 F and Texas Instrument Recorder was used.

RESULTS AND DISCUSSION

Thermal studies showed that the hydrated complexes began to evolve water in the 50—125°C temperature range. At temperatures between 100°C and 550°C, anhydrous complexes dissociated and, coupled with air oxidation, gave the metal oxides as residues. Table 1 contains the percentages of H_2O and metal oxide.

The non-isothermal decomposition of the metal chelates under study

TABLE 1

Analytical data for different metal–lapachol complexes

Complex	Residue	Percentage							
		C		H		H_2O		Metal oxide	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Y(C_{15}H_{13}O_3)_3 \cdot 1.5\ H_2O$	Y_2O_3	63.10	64.36	5.02	4.65	3.07	3.21	14.12	13.45
$In(C_{15}H_{13}O_3)_3 \cdot 1.5\ H_2O$	In_2O_3	61.62	63.17	4.16	4.56	3.04	3.19	16.46	16.34
$Sm(C_{15}H_{13}O_3)_3 \cdot H_2O$	Sm_2O_3	59.97	60.57	4.90	4.38	1.94	2.06	20.39	19.54
$Gd(C_{15}H_{13}O_3)_2 \cdot NO_3H_2O$	Gd_2O_3	50.62	50.02	4.34	3.61	2.26	2.50	25.54	25.24
$Dy(C_{15}H_{13}O_3)_2 \cdot NO_3\ 2.5\ H_2O$	Dy_2O_3	46.0	47.90	4.23	3.46	5.86	5.98	25.80	24.84

TABLE 2

Kinetic parameters for the pyrolytic decomposition of metal—lapachol chelates

Reaction	Temperature range (°C)	Methods *					
		A		B		C	
		E (kcal mole^{-1})	n	E (kcal mole^{-1})	n	E (kcal mole^{-1})	n
$Y(C_{15}H_{13}O_3)_3 \rightarrow$ Y_2O_3 + dissociation product	125—475	11.89	1.3	12.06	1	9.15	0.5
$In(C_{15}H_{13}O_3)_3 \rightarrow$ In_2O_3 + dissociation product	150—500	6.89	1.0	7.82	1	9.15	0.62
$Sm(C_{15}H_{13}O_3)_3 \rightarrow$ Sm_2O_3 + dissociation product	125—550	9.32	0.35	6.07	1	7.19	0.65
$Gd(C_{15}H_{13}O_3)_2NO_3 \rightarrow$ Gd_2O_3 + dissociation product	100—500	7.90	0.7	7.08	1	8.69	0.48
$Dy(C_{15}H_{13}O_3)_2NO_3 \rightarrow$ Dy_2O_3 + dissociation product	150—475	9.74	0.4	9.75	1	10.02	0.48

* A = Freeman and Carroll method.
B = Dave and Chopra method (DTG); eqn. (2) for first-order reaction.
C = Dave and Chopra method [eqn. (3)].

resembles the reaction of type $A_s \rightarrow B_s + C_g$ [5], which can be probed kinetically for evaluation of the kinetic parameters with the aid of the methods of Freeman and Carroll [eqn. (1)] and Dave and Chopra [eqns. (2) and (3)].

$$\frac{(-E/2.303R)\Delta T^{-1}}{\Delta \log(W_r)} = -n + \frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log(W_r)} \tag{1}$$

$$k = \frac{(-\mathrm{d}x/\mathrm{d}t)}{A - a} \text{(for first order reaction)} \tag{2}$$

$$\frac{(-E/2.303R)T^{-1}}{\log(A - a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A - a)} \tag{3}$$

where E = activation energy of the reaction; $\mathrm{d}w/\mathrm{d}t$ = rate of loss of weight; $W_r = W_c - W$, where W_c = weight loss at the completion of the reaction and W = weight loss at time t; $-\mathrm{d}x/\mathrm{d}t$ = the rate of loss of weight; A = total peak area under differential thermogravimetric curve; a = area at time t; and n = order of reaction.

A Freeman and Carroll plot (plot of $\Delta T^{-1}/\Delta \log W_r$ vs. $\Delta \log (\mathrm{d}w/\mathrm{d}t)/\Delta \log W_r$) resulted in a straight line in all reactions, the slope and intercept being equal to $-E/2.303R$ and n, respectively. For the sharper transition and the sample temperature to be more homogeneous, a sample weight ranging from 1 to 10 mg was taken for the thermogravimetric curves. Still more dependable values of E and n for the pyrolysis of the metal chelates of lapachol with Y(III), In(III), Sm(III), Gd(III) and Dy(III) could be obtained using the method of Dave and Chopra (DTG traces), which does not involve measurement of slopes of the thermogravimetric curves which are known to be sensitive [6]. Moreover, the points in the plot of $\mathrm{d}w/\mathrm{d}t$ vs. temperature (DTG traces) are joined by a smooth curve and the area enclosed is used in the calculations; thus the effect of small fluctuations due to heating rate and temperature variations in the original TG tracing is largely minimised.

Values of $\log K$, calculated from DTG curves for different reactions using Dave and Chopra's equation for a first order reaction, were plotted vs. the reciprocal of absolute temperature. A straight line was obtained for each reaction, indicating that the non-isothermal decomposition of the metal chelate follows first order kinetics.

Equation (3), which is similar in form to the Freeman and Carroll equation, was employed for kinetic parameters for different reactions. A plot of $T^{-1}/\log (A - a)$ vs. $\log (\mathrm{d}w/\mathrm{d}t)/\log (A - a)$ yielded a straight line, the slope and intercept being equal to $E/2.303R$ and n, respectively. Values of E and n associated with the non-isothermal decomposition of metal chelates of lapachol with Y(III), In(III), Sm(III), Gd(III) and Dy(III) obtained by different procedures are quite comparable (Table 2). The first step (desolvation of metal chelate) was too rapid to be studied.

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