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Note

KINETIC STUDIES OF THE NON-ISOTHERMAL DECOMPOSITION OF METAL CHELATES OF LAPACHOL WITH CALCIUM(II), BARIUM(II) AND LEAD(II)

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Lapachol forms co-ordination complexes with metal ions [1]. Earlier, Bhatia and Sawhney [2,3] reported the pyrolytic decomposition of chelates of lapachol with Be(II), ZrO(II), Pd(II), Ti(III), Y(III), In(III), Sm(III), Gd(III) and Dy(III). The present paper deals with the evaluation of the kinetic parameters of the non-isothermal decomposition of anhydrous chelates of lapachol with Ca(II), Ba(II) and Pb(II) using the methods of Freeman and Carroll [4] and Dave and Chopra [5].

EXPERIMENTAL

Metal chelates were isolated by the procedure reported earlier [3]. Thermogravimetric evaluation of metal chelates was carried out on a Cahn balance equipped with a Fischer furnace and programmer. Air-dried samples were subjected to a continuous steady increase in temperature (10°C min^{-1}).

RESULTS AND DISCUSSION

Thermal investigations showed that hydrated chelates lose water in the temperature range 60–190°C. Between 190 and 860°C anhydrous chelates pyrolysed and in the presence of atmospheric oxygen, gave the corresponding metal oxide as the residue. Table 1 records the percentages of water and metal oxide obtained from the hydrated chelates.

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TABLE I

Analytical data

Complex	Residue	Oxide (%)		Water (%)	
		Found	Calcd.	Found	Calcd.
$Ca(C_{15}H_{13}O_3)NO_3 \cdot 1.75\ H_2O$	CaO	15.04	14.95	8.26	8.41
$Ba(C_{15}H_{13}O_3)NO_3 \cdot 1.5\ H_2O$	BaO	32.88	32.81	5.85	5.75
$Pb(C_{15}H_{13}O_3)_2 \cdot 0.5\ H_2O$	PbO	32.14	31.97	1.19	1.28

The decomposition of metal chelates under investigation resembles the reaction $A_s \rightarrow B_s + C_g$ [4]

which could be probed kinetically for evaluation of the kinetic parameters using the methods of Freeman and Carroll and Dave and Chopra.

A Freeman and Carroll plot [plot of $\Delta T^{-1}/\Delta \log W_r$ vs. $\log(dw/dt)/\Delta \log w_r$] resulted in a straight line in all cases, the slope and intercept being equal to $-E/2.303R$ and n, respectively. In order to obtain a sharper transition and more homogeneous sample temperatures, the smallest possible amount (1–10 mg) of sample was used for pyrolysis. More reliable values for n, E and Z (collision number) could be obtained by Dave and Chopra methods that do not involve measurement of slopes of thermogravimetric curves, which are known to be sensitive [6]. Values of $\ln k$ calculated from the Dave and Chopra expression assuming $n = 1$

$$k = \frac{\frac{A}{m_0}^{(n-1)} - \frac{dx}{dt}}{(A-a)^n}$$

(where the various terms have the usual meaning) were plotted against the reciprocal of absolute temperature. The slope of the straight line so obtained gave the value of activation energy (E) for the reaction.

Another expression due to Dave and Chopra viz. plot of $T^{-1}/\log(A-a)$ vs. $\log(dx/dt)/\log(A-a)$ was a straight line, the slope and intercept of which could also be used for the evaluation of n and E. Table 2 reveals that the values of n and E obtained from different methods were quite comparable. Further, small values of Z suggest that the pyrolytic decomposition of the complexes is slow.

TABLE 2

Kinetic parameters for the pyrolytic decomposition of metal-lapachol chelates

Reaction	Temp. range (°C)	Method						
		A		B			C	
		E (kcal mole^{-1})	n	E (kcal mole^{-1})	n	Z	E (kcal mole^{-1})	n
$Ca(C_{15}H_{13}O_3)NO_3 \rightarrow$ CaO + dissociation product	220–720	4.6658	1.15	4.8048	1	1.32	4.576	0.69
$Ba(C_{15}H_{13}O_3)NO_3 \rightarrow$ BaO + dissociation product	200–860	4.1184	0.6	4.576	1	1.32	3.8896	0.60
$Pb(C_{15}H_{13}O_3)_2 \rightarrow$ PbO + dissociation product	200–860	4.2900	0.4	4.862	1	1.12	4.576	0.65

A = Freeman and Carroll method.

B and C = Dave and Chopra method for first- and second-order reaction, respectively.

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