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Note

KINETIC ANALYSIS OF DERIVATIVE THERMOGRAVIMETRIC DATA OF 5-HYDROXY-1,4-NAPHTHOQUINONE (JUGLONE) AND SOME OF ITS DIVALENT METAL CHELATES

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Previous papers [1–5] regarding kinetic analysis of the non-isothermal decomposition of metal complexes of hippuric acid, naphthoquinone and acetophenone derivatives have been reported from this laboratory. The literature reveals that Bottei and McEachern [6] synthesised and characterised spectrally and thermally some metal chelates of juglone with a general formula $MR_n \cdot xH_2O$, where M = Cu, Pb, Ni, Co and Zn and $x = 0$, 0, 2, 2 and 2, respectively. The pyrolytic decomposition of these chelates has still to be investigated. Attempts at the kinetic analysis of the derivative thermogravimetric data of these chelates using the Dave–Chopra equations, eqns. (1) and (2), are made here.

$$k = \frac{(A/m_0)^{n-1}(-\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{1}$$

$$-\frac{(E/2.303R)(T^{-1})}{\log(A-a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A-a)} \tag{2}$$

Where A is the total area under the differential thermogravimetric curve, a is the area for the reaction curve at time t, $\mathrm{d}x/\mathrm{d}t$ is the height of the curve at time t, m_0 is the initial mole fraction of the reactant and n is the order of reaction with respect to the reactant.

EXPERIMENTAL

All chemicals were of reagent grade. Juglone was obtained from Aldrich Chemical Company, U.S.A., and is metal chelates were prepared according to the procedure adopted by Bottei and McEachern [6]. Elemental analysis of the metal chelates agreed with the composition proposed by Bottei and McEachern. For thermal analysis, a DuPont instrument was used. Thermograms were obtained in a nitrogen atmosphere. The heating rate (5° min^{-1}) was constant for all runs.

TABLE I

Kinetic parameters of the pyrolytic decomposition of juglone and its metal chelates

Reactions [a]	Temp. range (°C)	Method				
		Eqn. (1)			Eqn. (2)	
		n	E (kcal mole^{-1})	Z	n	E (kcal mole^{-1})
$C_{10}H_6O_3 \rightarrow$ Carbon + volatile products	180–440	1	13.73	0.35	0.68	16.02
$CuL_2 \rightarrow CuO$ + dissociation products	324–364	1	98.38	0.39	0.45	228.80
$PbL_2 \rightarrow Pb_3O_4$ + dissociation products	249–400	1	13.73	0.10	0.51	19.07
$NiL_2 \cdot 2\,H_2O \rightarrow NiL_2 + 2\,H_2O$	176–246	1	50.34	0.32	0.45	86.40
$NiL_2 \rightarrow NiO$ + dissociation products	300–392	1	36.61	0.25	0.61	59.49
$CoL_2 \cdot 2\,H_2O \rightarrow CoL_2 + 2\,H_2O$	148–232	1	18.31	0.19	0.39	36.61
$CoL_2 \rightarrow Co_3O_4$ + dissociation products	300–376	1	25.63	0.39	0.55	34.32
$ZnL_2 \cdot 2\,H_2O \rightarrow ZnL_2 + 2\,H_2O$	124–308	1	7.78	0.14	0.41	15.24
$ZnL_2 \rightarrow ZnO$ + dissociation products	332–440	1	22.88	0.25	0.50	34.32

[a] $L = C_{10}H_5O_3$

RESULTS AND DISCUSSION

Since it is difficult in practice to maintain constant such variables as heating rate, temperature variation, etc., which appear to be significant factors for kinetic data if slope-dependent procedures are adopted, the non-isothermal decomposition of metal chelates of juglone with Cu, Pb, Ni, Co and Zn has been investigated kinetically using the Dave–Chopra procedures, which have been stated to give dependable kinetic data even if slight fluctuations in the above variables have been observed [7].

The reaction under consideration involves solid state decomposition where one product remains in the solid state while another is volatile [8].

$$A_s \rightarrow B_s + C_g$$

Assuming $n = 1$, values of $\log k$, calculated from eqn. (1) and DTG curves, were plotted against the reciprocal of the absolute temperature. A straight line relationship was obtained in all cases, which supports the view that the non-isothermal decomposition of metal chelates follows first-order kinetics. The slope ($-E/2.303R$) and the intercept ($\log Z$) of the graph yielded values for the activation energy (E) and the frequency factor (Z) of the reaction.

Equation (2) has also been utilised for kinetic parameters for those reactions. A plot of $(1/T)/\log(A-a)$ vs. $\log(dx/dt)/\log(A-a)$ for all reactions gave a straight line. Values of E (energy of activation) and n (order of reaction) were calculated from the slope ($-E/2.303R$) and the intercept (n) of the straight line.

Table 1 gives the values of the kinetic parameters of the pyrolytic decomposition of juglone and its metal chelates. Abnormally low values of Z led us to believe that the non-isothermal decomposition of the juglone and its metal chelates is a slow process.

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