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Note

KINETICS OF THE PYROLYTIC DECOMPOSITION OF SOME METAL COMPLEXES OF 2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHALENEDIONE (LAPACHOL) FROM DTG CURVES

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Sawhney et al. [1–3] investigated the kinetics of the non-isothermal decomposition of metal complexes of naphthoquinone, acetophenone and glycine derivatives using the Dave–Chopra method [4]. This note concerns the estimation of the kinetic parameters of the pyrolytic decomposition of some metal complexes of lapachol with calcium, barium, cadium, oxovanadium, lead and cerium(IV) with the aid of Dave–Chopra expressions [1,2]

$$k = \frac{(-\mathrm{d}x/\mathrm{d}t)}{A-a} \quad \text{(for first-order reaction)} \tag{1}$$

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

EXPERIMENTAL

All the reagents used were of B.D.H./Aldrich quality. For isolation of metal complexes in the solid state, sodium lapacholate was added with constant stirring to

TABLE 1

Analytical data

Complex	C (%)		H (%)	
	Found	Calcd.	Found	Calcd.
$Ca(C_{15}H_{13}O_3)NO_3 \cdot 1.75\ H_2O$	47.86	48.05	5.21	4.90
$Ba(C_{15}H_{13}O_3)NO_3 \cdot 1.5\ H_2O$	39.31	38.51	2.98	3.42
$Cd(C_{15}H_{13}O_3)_2 \cdot 0.75\ H_2O$	59.83	59.32	5.02	4.53
$Ce(C_{15}H_{13}O_3)_2(NO_3)_2 \cdot 3.5\ H_2O$	52.95	52.54	4.99	4.82
$VO(C_{15}H_{13}O_3)_2 \cdot 1.5\ H_2O$	62.99	62.51	5.73	5.04
$Pb(C_{15}H_{13}O_3)_2 \cdot 0.5\ H_2O$	52.01	51.66	4.17	3.87

TABLE 2

Thermogravimetric results

Stable phase and Temp. range	Loss % and Temp. range	Loss %		Metal oxide %	
		Found	Calcd.	Found	Calcd.
$Ca \cdot C_{15}H_{13}O_3 \cdot NO_3 \cdot 1.75\ H_2O$ up to 60°C					
$Ca \cdot C_{15}H_{13}O_3 \cdot NO_3$ ca. 190–220°C	$1.75\ H_2O$ 60–190°C	8.26	8.41		
CaO 720–800°C				15.04	14.95
$Ba \cdot C_{15}H_{13}O_3 \cdot NO_3 \cdot 1.5\ H_2O$ up to 60°C					
$Ba \cdot C_{15}H_{13}O_3 \cdot NO_3$ 170–200°C	$1.5\ H_2O$ 60–170°C	5.85	5.75		
BaO 860–900°C				32.88	32.81
$Cd \cdot (C_{15}H_{13}O_3)_2 \cdot 0.75\ H_2O$ up to 68°C					
$Cd(C_{15}H_{13}O_3)_2$ 108–132°C	$0.75\ H_2O$ 68–108°C	2.10	2.06		
$Cd(C_{15}H_{13}O_3)_{13/16}$ 500–560°C	$19/16\ (C_{15}H_{13}O_3)$ 480–500°C	46.15	47.15		
CdO 740–800°C				21.67	21.17
$Ce(C_{15}H_{13}O_3)_2(NO_3)_2 \cdot 3.5\ H_2O$ up to 60°C					
$Ce(C_{15}H_{13}O_3)_2 \cdot (NO_3)_2$ 220–260°C	$3.5\ H_2O$ 60–220°C	8.93	9.19		
$Ce(C_{15}H_{13}O_3)_{3/2} \cdot (NO_3)_2$ 340–380°C	$1/2\ (C_{15}H_{13}O_3)$ 260–340°C	17.26	17.58		
$Ce(C_{15}H_{13}O_3)_{1/16}(NO_3)_2$	$23/16\ (C_{15}H_{13}O_3)$	50.00	50.56		
CeO_2 760–800°C				25.59	25.12
$VO(C_{15}H_{13}O_3)_2\ 1.5\ H_2O$ up to 70°C					
$VO(C_{15}H_{13}O_3)_2$ 180–220°C	$1.5\ H_2O$ 70–180°C	4.54	4.68		
$Pb(C_{15}H_{13}O_3)_2\ 0.5\ H_2O$ up to 80°C					
$Pb(C_{15}H_{13}O_3)_2$ 100–200°C	$0.5\ H_2O$ 80–100°C	1.19	1.28		
PbO 860–900°C				32.14	31.97

TABLE 3

Kinetic parameters of the non-isothermal decomposition of some metal complexes of lapachol

Reaction	Temp. range (°C)	Eqn.				
		(1)			(2)	
		n	E	Z	n	E
$Ca\cdot R\cdot NO_3\cdot 1.75\ H_2O \rightarrow Ca\cdot R\cdot NO_3 + 1.75\ H_2O$	60–110	1	9.84	1.29	0.52	5.96
$Ca\cdot R\cdot NO_3 \rightarrow$ CaO + dissociation products	220–720	1	4.63	0.05	0.57	1.39
$Ba\cdot R\cdot NO_3\cdot 1.5\ H_2O \rightarrow Ba\cdot R\cdot NO_3 + 1.5\ H_2O$	60–170	1	19.87	1.58	0.80	23.84
$Ba\cdot R\cdot NO_3 \rightarrow$ BaO + dissociation products	200–860	1	3.97	0.04	0.62	1.59
$Cd\cdot R_2\cdot 3.5\ H_2O \rightarrow Cd\cdot R_2 + 3.5\ H_2O$	68–108	1	32.98	0.74		
$Cd\cdot R_2 \rightarrow Cd\cdot R_{13/16} + 19/17$ organic matter	132–500	1	5.96	0.71	0.6	1.98
$Cd\cdot R_{13/16} \rightarrow$ CdO + dissociation products	560–740	1	19.87	1.41	0.61	14.90
$Ce\cdot R_2(NO_3)_2\ 3.5\ H_2O \rightarrow Ce\cdot R_2(NO_3)_2 + 3.5\ H_2O$	60–220	1	8.44	2.34	0.61	7.95
$Ce\cdot R_2(NO_3)_2 \rightarrow Ce\cdot R_{3/2}(NO_3)_2 + 0.5\ R$	260–340	1	49.68	2.13		
$Ce\cdot R_{3/2}(NO_3)_2 \rightarrow Ce\cdot R_{1/16}(NO_3)_2 + 23/16\ R$	380–592	1	13.90	1.65	0.75	8.28
$Ce\cdot R_{1/16}(NO_3)_2 \rightarrow CeO_2$ + dissociation products	600–760	1	25.83	1.65	–	–
$VO\cdot R_2\cdot 1.5\ H_2O \rightarrow VO\cdot R_2 + 1.5\ H_2O$	70–180	1	10.13	1.58	0.73	13.25
$VO\cdot R_2 \rightarrow V_2O_5$ + dissociation products	220–840	1	4.97	0.06	0.59	2.15
$Pb\cdot R_2\cdot 0.5\ H_2O \rightarrow Pb\cdot R_2 + 0.5\ H_2O$	80–100					
$Pb\cdot R_2 \rightarrow$ PbO + dissociation products	200–860	1	4.97	0.34	0.62	3.97

$R = C_{15}H_{13}O_3$; n = order of reaction; E = energy of activation (kcal mole^{-1}); Z = collision number.

the metal solution. The coloured precipitate was filtered, washed with double distilled water and dried at 45°–50°C. Table 1 contains elemental analysis data collected using THERELEC. Air-dried samples were pyrolysed at the heating rate of 10°C min^{-1} for all the runs in a modern thermogravimetric balance with Toshniwal furnace in air.

RESULTS AND DISCUSSION

Table 2 incorporates the thermogravimetric results together with analytical data. Thermolysis curves for all the metal complexes showed two or more sigmoidal traces. The separate sigmoidal traces were analyzed for values of kinetic parameters using methods similar to those employed for the TG curve having one sigmoid. Pyrolytic decomposition of the complexes resembles the reaction [5]

$$A_s \rightarrow B_s + C_g$$

which can be kinetically probed.

Values of A, a, and dx/dt were calculated corresponding to different temperatures from DTG curves. A plot of log k vs. T^{-1} yielded a straight line in all cases, indicating that non-isothermal desolvation/decomposition follows first-order kinetics, the slope and intercept provided the values of E and Z (collision number), respectively. Using eqn. (2), E and n were also calculated. Plots of $T^{-1}/\log(A-a)$ vs. $\log(dx/dt)/\log(A-a)$ for all sigmoids, except those of the temperature ranges: Cd complex, 68–100°C, Ce complex, 260–340°C and 600–760°C, and Pb complex, 80–100°C, gave straight lines. Desolvation of the lead complex was too fast to be studied. Table 3 contains the values of the kinetic parameters due to both equations.

As the pyrolysis of the complexes was carried out with a manually-operated assembly, factors such as heating rate, temperature variance, etc, which contribute significantly to kinetic studies if slope-dependent procedures [6,7] are employed, could not be kept reasonably constant. Under such conditions only the Dave–Chopra procedure together with DTG curves could give dependable values of kinetic parameters as it does not involve the slope of TG curves. Moreover, the plots (dx/dt vs. temperature) are joined by smooth curves and enclosed areas are used for calculations; hence the effect of small fluctuations in original TG tracings is largely minimized. The decomposition reactions under study appear to be slow processes as the collision numbers have abnormally low values (Table 3).

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