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Note

KINETIC STUDIES ON THE NON-ISOTHERMAL DECOMPOSITION OF SOME METAL COMPLEXES OF LAPACHOL AND JUGLONE

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Sawhney et al. [1—3] probed kinetically some reactions including the pyrolytic decomposition of metal complexes of lapachol with Y(III), In(III), Sm(III), Gd(III) and Dy(III) with the aid of the procedures of Freeman and Carroll [4] and Dave and Chopra [5]. The present communication concerns the evaluation of the kinetic parameters of decomposition of anhydrous metal complexes of lapachol with Be(II), ZrO(II), Pd(II) and Ti(III), and of juglone with Cd(II), Y(III) and Sm(III) using the above methods.

EXPERIMENTAL

All chemicals used were either of B.D.H. or Aldrich AnalaR quality. For isolation of the metal chelates in the solid state, the procedure reported in an earlier communication [1] was adopted. For C and H analysis, THERELEC was employed. The theoretical and experimental values for the percentages of C and H tallied. A Cahn electrobalance equipped with a Fischer furnace, Fischer temperature programmer and Texas recorder was employed for the thermal decomposition studies. Air-dried samples were subjected to a continuous increase in temperature. The heating rate (5°C min^{-1}) was constant for all the runs, except in the case of the Cd(II)—juglone complex, for which it was 7°C min^{-1}.

RESULTS AND DISCUSSION

Thermal investigations revealed that hydrated complexes began to evolve water in the temperature range 50—125°C. Between 50 and 900°C, anhydrous complexes dissociated and, coupled with air oxidation, gave metal oxide as residues. Table 1 contains the analytical data.

Decomposition of anhydrous complexes is of the type $A_s \rightarrow B_s + C_g$, which could be kinetically probed using the expressions of Freeman and Carroll, and Dave and Chopra. A plot of Freeman and Carroll (ΔT^{-1}/

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TABLE 1

Analytical data

Complex	Colour	Residue	Percentage			
			Oxide		Water	
			Found	Calcd.	Found	Calcd.
$Be(C_{15}H_{13}O_3)_2$	Yellow	BeO	5.0	5.09		
$ZrO(C_{15}H_{13}O_3)_2 \cdot Cl_2H_2O$	Red	ZrO_2	19.20	18.17	2.41	2.65
$Pd(C_{15}H_{13}O_3)_2$	Dark grey	PdO	23.42	24.54		
$Ti(C_{15}H_{13}O_3)_3$	Yellow	Ti_2O_3	9.75	9.32		
$Cd(C_{10}H_5O_3)_2 \cdot 0.25\ H_2O$	Rusty brown	CdO	27.76	27.60	1.04	0.97
$Y(C_{10}H_5O_3)_3$	Red	Y_2O_3	19.29	18.57		
$Sm(C_{10}H_5O_3)_3$	Rusty brown	Sm_2O_3	25.06	25.04		

TABLE 2

Kinetic parameters for the pyrolytic decomposition of metal—lapachol and metal—juglone chelates

Reaction	Temp. range (°C)	Method [a]					
		A		B		C	
		E (kcal mole^{-1})	n	E (kcal mole^{-1})	n	E (kcal mole^{-1})	n
$Be(C_{15}H_{13}O_3)_2 \rightarrow Be(C_{15}H_{13}O_3)_{0.5}$ + dissociation product	100—350	4.16	0.9	4.24	1	4.12	0.73
$ZrO(C_{15}H_{13}O_3)_2Cl_2 \rightarrow ZrO_2$ + dissociation product	150—550	7.32	0.8	6.89	1	7.18	0.53
$Pd(C_{15}H_{13}O_3)_2 \rightarrow PdO$ + dissociation product	225—550	13.72	0.1	13.13	1	15.50	0.68
$Ti(C_{15}H_{13}O_3)_3 \rightarrow Ti(C_{15}H_{13}O_3)_{1.4}$ + dissociation product	75—225	12.36		10.28	1	16.47	0.89
$Ti(C_{15}H_{13}O_3)_{1.2} \rightarrow Ti_2O_3$ + dissociation product	375—550	45.76	0.8	29.29	1	13.73	0.29
$Cd(C_{10}H_5O_3)_2 \rightarrow CdO$ + dissociation product	150—900	4.86	0.1	3.03	1	2.70	0.42
$Y(C_{10}H_5O_3)_3 \rightarrow Y(C_{10}H_5O_3)_{1.8}$ + dissociation product	50—225	4.23	0.4	11.38	1	11.04	1.40
$Y(C_{10}H_5O_3)_{1.8} \rightarrow Y(C_{10}H_5O_3)_{0.2}$ + dissociation product	250—550	10.56	0.3	14.32	1	16.47	0.90
$Sm(C_{10}H_5O_3)_3 \rightarrow Sm(C_{10}H_5O_3)_{1.25}$ + dissociation product	50—175	2.90	0.3	6.49	1	6.66	1.09
$Sm(C_{10}H_5O_3)_{1.25} \rightarrow Sm_2O_3$ + dissociation product	225—400	26.80	0.8	21.08	1	21.35	0.90

[a] Method of A, Freeman and Carroll; B, Dave and Chopra (DTG); and C, Dave and Chopra.

$\Delta \log W_r$) vs. $\Delta \log(dw/dt)/\Delta \log W_r$ yielded fairly good straight lines; the slope and intercept gave $-E/2.303R$ and n, respectively. Small samples (1—10 mg) were used for pyrolysing the complexes in order to obtain a sharper transition and for the sample temperature to be homogeneous.

Dave and Chopra could give more reliable values for n, E and Z (collision number) even if the ideal conditions, which must be maintained while pyrolysing metal complexes [6] applying the method of Freeman and Carroll, undergo small deviations [5]. Assuming $n = 1$, the values of $\log k$ corresponding to various temperatures were calculated using the expression of Dave and Chopra

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

(where the terms have their usual meaning) and plotted against the reciprocal of absolute temperature. The straight line so obtained, in all cases, supported the assumption. The slope of the straight line gave the activation energy, E, for the reaction.

Values of n and E for the non-isothermal decomposition of metal complexes have also been estimated by another expression due to Dave and Chopra [1]. A plot of $T^{-1}/\log(A-a)$ vs. $\log(dx/dt)/\log(A-a)$ gave straight lines for all the reactions; the slope and intercept could be used to obtain n and E values, respectively. Table 2 reveals that the values of n and E could be reasonably compared. The non-isothermal dissolvation of solvated oxozirconium—lapacholate and cadmium—juglonate was too fast to be studied kinetically.

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