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Note

KINETICS OF DESOLVATION OF SOLVATED METAL COMPLEXES OF HIPPURIC ACID AND LAPACHOL FROM THERMOGRAVIMETRIC CURVES

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Several dehydration reactions [1—8] have been kinetically studied using the Freeman—Carroll procedure [9]. The Dave—Chopra procedure [10] together with the DTG curve has found limited application. An attempt, the reference to which is not available, has been made in this note to probe kinetically the desolvation of solvated metal complexes of hippuric acid with Er(III), Ce(III) and Nd(III), and lapachol[2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone] with Fe(II), Ni(II), UO_2(II), Fe(III), Cr(III) and Al(III) using the Freeman—Carroll, eqn. (1), and Dave—Chopra, eqn. (2), equations.

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

$$k = \frac{(A/m_0)^{n-1}(-\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \quad (2)$$

where the terms have their usual meanings.

EXPERIMENTAL

All the reagents employed were of analytical grade.

For the isolation of metal lapacholates and hippurates in the solid state, a solution of sodium hippurate/lapacholate was added slowly with constant stirring to the metal solution. The precipitate was collected on a sintered crucible, washed several times with distilled water and dried at 50—60°C. Elemental analysis data collected on a Perkin-Elmer 240 B tallied with the theoretical values.

Air dried metal complexes were pyrolysed on a Modern Thermogravimetric Balance with a Toshiniwal furnace at the rate of 6°C min^{-1} and with continuous increase of temperature.

RESULTS AND DISCUSSION

In the investigation of metal complexes of general formula $M(R)_n \cdot x\,H_2O$, where M = Ni(II), Fe(II), UO_2(II), Fe(III), Cr(III), Al(III), R =

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$C_{15}H_{13}O_3$ and M = Er(III), Ce(III), Nd(III), R = $C_6H_5CONHCH_2COO$, n = 2 or 3 and x = 0—5, it was found that the hydrated compounds began to evolve water in the temperature range 68—200°C. At temperatures between 132 and 780°C, the anhydrous complexes dissociated and, coupled with oxidation, gave metal oxide residues.

Desolvation of metal complexes

$$M(R)_n \cdot x\ H_2O(s) \rightarrow M(R)_n(s) + x\ H_2O\ (vapours)$$

resembles the type:

$$A_s \rightarrow B_s + C_g$$

which could be kinetically probed with the said procedure [9,10].

Values of dw/dt, W_r and T^{-1} were derived from the graph of the first derivative of the TG curve (dw/dt) and the weight of reactant (W_r) as a function of the reciprocal of absolute temperature. A plot of $\Delta T^{-1}/\Delta \log W_r$ vs.

$\Delta \log(dw/dt)/\Delta \log W_r$ yielded a straight line in each case, the slope and intercept of which corresponded to $-E/2.303R$ and n, respectively.

The literature reveals that all the documented procedures involving TG curves involve precise temperature control for kinetic experiments which is much more difficult with TG than with isothermal methods. The Dave—Chopra procedure does not involve the slope of the TG curve which influences the kinetic data. Moreover the Dave—Chopra procedure is associated with the DTG curve (dw/dt vs. temperature) in which the points are joined by a smooth curve and the areas enclosed therein are used in calculations, minimising thereby the effect of small fluctuations due to heating rate and temperature variations in TG traces. The plot of log k calculated from eqn.

TABLE 1

Kinetic data for the non-isothermal desolvation of solvated metal complexes of hippuric acid and lapachol

Reaction	Methods			
	Freeman—Carroll		Dave-Chopra	
	E (kcal mole^{-1})	n	E (kcal mole^{-1})	n
R = $C_{15}H_{13}O_3$				
$Fe(R_2) \cdot 2\ H_2O \rightarrow Fe(R_2) + 2\ H_2O$	40.27	1.2	45.80	1
$Ni(R_2) \cdot 2.5\ H_2O \rightarrow Ni(R_2) + 2.5\ H_2O$	7.55	0.87	34.42	1
$UO_2(R_2) \cdot 0.5\ H_2O \rightarrow UO_2(R_2) + 0.5\ H_2O$	10.98	0.97		
$Fe(R_3) \cdot 2\ H_2O \rightarrow Fe(R_3) + 2\ H_2O$	32.03	1.05	28.60	1
$Cr(R_3) \cdot 0.75\ H_2O \rightarrow Cr(R_3) + 0.75\ H_2O$	27.47	1.15	27.47	1
$Al(R_3) \cdot 1.25\ H_2O \rightarrow Al(R_3) + 1.25\ H_2O$	19.45	0.8	14.41	1
R = $C_6H_5CONHCH_2COO$				
$Ce(R_3) \cdot 4.5\ H_2O \rightarrow Ce(R_3) + 4.5\ H_2O$	10.53	0.8	11.44	1
$Nd(R_3) \cdot 4\ H_2O \rightarrow Nd(R_3) + 4\ H_2O$	27.46	1.25	12.81	1
$Er(R_3) \cdot 4.5\ H_2O \rightarrow Er(R_3) + 4.5\ H_2O$	21.74	0.66	22.88	1

(2), assuming $n = 1$ for pyrolytic desolvation of solvated metal complexes, against $1/T$ gave a straight line: it shows that the pyrolytic desolvation of the complexes follows first-order kinetics extending support to the data due to the Freeman—Carroll method.

Table 1 gives the kinetic data.

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