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Note

THE KINETICS OF NON-ISOTHERMAL DECOMPOSITION OF METAL COMPLEXES OF HIPPURIC ACID WITH Cu(II), Cd(II), Pb(II), Fe(III) AND Pr(III)

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The literature reveals that the non-isothermal decomposition of metal complexes of hippuric acid has not been kinetically probed. This communication concerns the evaluation of the kinetic parameters of the pyrolytic decomposition of metal complexes of hippuric acid with Cu(II), Cd(II), Pb(II), Fe(III) and Pr(III) using the procedures of Freeman and Carroll [1], and Dave and Chopra [2].

EXPERIMENTAL

All the reagents used were of B.D.H. quality. For isolation of the metal complexes in the solid state, sodium hippurate was added, with constant stirring, to the metal solution. The solution mixture was refluxed for 1 h and allowed to stand. The precipitate was filtered and washed with ice-cooled water and dried at 35—40° C. The dark blue coloured crystals of the copper—hippuric acid complex, Cu $(C_6H_5CONHCH_2COO)_2 \cdot 4\ H_2O$, were recrystallised from MeOH to obtain light blue crystals, Cu $(C_6H_5CONHCH_2COO)_2 \cdot H_2O$ [3]. Table 1 contains elemental analysis data collected using THERELEC. For thermogravimetric curves of the metal complexes, samples were first air-dried and then pyrolysed in a modern thermogravimetric balance with a Toshniwal furnace. The instrument was standardised with calcium oxalate. The heating rate was 10° C min^{-1} for all runs.

RESULTS AND DISCUSSION

The pyrolytic curves revealed the observed percentage weight losses in dark blue or light blue copper complexes, cadmium, lead and praseodymium complexes, in the temperature ranges: 60—200° C or 60—120° C, 60—180° C, 44—160° C and 64—180° C, as 15, 4.89, 7.97, 7.60 and 9.43, respectively, which correspond to the loss of 4 H_2O, H_2O, 2 H_2O, 2.5 H_2O and 4 H_2O. The thermal stability data show that the decomposition of anhydrous complexes started at 240° C (CuR_2 from $CuR_2 \cdot 4\ H_2O$, dark blue), 140° C (CuR_2 from $CuR_2 \cdot H_2O$, light blue), 196° C (CdR_2), 220° C (PbR_2), 220° C (PrR_3) and

TABLE 1

Analytical data

Complex *	Colour	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$CuR_2 \cdot 4\,H_2O$	Dark blue	12.52	12.91	44.32	43.95	5.40	4.88	5.31	5.69
$CuR_2 \cdot H_2O$	Light blue	14.29	14.51	48.66	49.37	4.32	4.11	6.83	6.40
$CdR_2 \cdot 2\,H_2O$	White	21.20	22.20	42.57	42.82	4.84	4.76	5.59	5.55
$PbR_2 \cdot 2.5\,H_2O$	White	34.46	34.07	35.61	35.51	3.39	3.45	4.39	4.60
FeR_3	Brick red	9.37	9.49	55.41	54.92	4.52	4.07	7.48	7.12
$PrR_3 \cdot 4\,H_2O$	Dirty white	18.54	18.86	43.55	43.38	4.45	4.28	5.81	5.62

* $R = C_6H_5CONHCH_2COO$.

80°C (FeR_3), where R = $C_6H_5CONHCH_2COO$.

In the iron complex, the TG curve followed a simple sigmoidal path whereas two or more sigmoids were observed in the TG curves of the other complexes. The separate sigmoidal traces were analysed for values of kinetic parameters using methods similar to those employed for the TG curve having one sigmoid.

The non-isothermal decomposition of the metal complexes under study resembles the reaction

$A_s \rightarrow B_s + C_g^1$

which can be kinetically probed for kinetic parameters using the expressions of Freeman and Carroll (1) and Dave and Chopra (2,3).

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

$$k = \frac{(-\mathrm{d}x/\mathrm{d}t)}{A - a} \text{ (for first-order reaction)} \tag{2}$$

$$\frac{(-E/2.303R)(T^{-1})}{\log(A - a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A - a)} \tag{3}$$

where E is the activation energy of the reaction; $\mathrm{d}w/\mathrm{d}t$ is the rate of loss of weight; $W_r = Wc - W$, where W_c is the weight loss at the completion of the reaction and W is the weight loss at time t; $-\mathrm{d}x/\mathrm{d}t$ is the rate of loss of weight; A is the total peak area under the differential thermogravimetric curves; a is the area at time t, and n is the order of the reaction.

On plotting $\Delta T^{-1}/\Delta \log W_r$ vs. $\log(\mathrm{d}w/\mathrm{d}t)/\log W_r$ (Freeman and Carroll), a straight line is obtained, the slope and intercept of which correspond to $-E/2.303\ R$ and n, respectively. Small samples were used to maintain a constant heating rate. The method of Dave and Chopra, involving DTG curves, could give more dependable values of kinetic parameters because it does not involve the measurement of slopes of TG curves, which are known to be sensitive [4]. In addition, the effect of small fluctuations due to heating rate and temperature variation in the original TG trace is largely minimised as the points in the plot of $\mathrm{d}w/\mathrm{d}t$ vs. temperature (DTG curve) are joined by a smooth curve and the enclosed area is used in the calculations [eqns. (2) and (3)].

Using eqn. (2), values of log k were calculated from DTG curves, and plotted against the reciprocal of absolute temperature. A straight line followed, indicating that non-isothermal desolvation/decomposition follows first-order kinetics. A plot of $T^{-1}/\log (A - a)$ vs. $\log (\mathrm{d}x/\mathrm{d}t)/\log(A - a)$ for all the reactions [eqn. (3)] gave a straight line, from the slope ($-E/2.303\ R$) and the intercept (n) of which E and n could be obtained.

Table 2 contains the values of the kinetic parameters for the pyrolytic decomposition of metal complexes of hippuric acid. It is seen that the values obtained using the different procedures are quite comparable. The activation energies for the pyrolytic decomposition of iron and praseodymium com-

TABLE 2

Values of E (energy of activation) and n (order of reaction) for the different reactions

Reaction *	Method					
	A		B		C	
	$\bar{n}$	E (kcal $mole^{-1}$)	$\bar{n}$	E (kcal $mole^{-1}$)	$\bar{n}$	E (kcal $mole^{-1}$)
$CuR_2 \cdot 4\ H_2O \rightarrow CuR_2 + 4\ H_2O$	0.90	14.63	1	14.44	0.93	13.73
$CuR_2 \rightarrow CuR_{1/2} + R_{3/2}$	0.80	45.76	1	28.60	0.84	38.90
$CuR_{1/2} \rightarrow CuR_{5/16} + R_{3/16}$	0.85	21.74	1	22.88	0.40	27.46
$CuR_{5/16} \rightarrow CuO +$ dissociation product	0.90	274.46	1	271.71	—	—
$CuR_2 \cdot H_2O \rightarrow CuR_2 + H_2O$	0.60	16.78	1	16.90	0.93	16.02
$CuR_2 \rightarrow CuR_{1/2} + R_{3/2}$	0.70	13.73	1	10.17	0.74	11.77
$CuR_{1/2} \rightarrow CuO +$ dissociation product	0.34	9.15	1	9.15	0.38	8.85
$CdR_2 \cdot 2\ H_2O \rightarrow CdR_2 + 2\ H_2O$	0.36	7.32	1	8.17	0.50	10.98
$CdR_2 \rightarrow CdO +$ dissociation product	0.50	12.58	1	12.71	0.70	12.06
$PbR_2 \cdot 2.5\ H_2O \rightarrow PbR_2 + 2.5\ H_2O$	0.50	9.92	1	9.15	0.58	9.47
$PbR_2 \rightarrow PbR + R$						
$PbR \rightarrow Pb_3O_4 +$ dissociation product	0.30	9.15	1	9.84	0.55	9.15
$FeR_3 \rightarrow Fe_2O_3 +$ dissociation product	0.40	10.68	1	4.09	0.53	4.58
$PrR_3 \cdot 4\ H_2O \rightarrow PrR_3 + 4\ H_2O$	0.40	5.72	1	14.30	0.60	18.30
$PrR_3 \rightarrow Pr_2O_3 +$ dissociation product	0.50	12.20	1	16.41	0.70	14.30

* R = $C_6H_5CONHCH_2COO$.

** A = Freeman and Carroll method; B = Dave and Chopra method (DTG). Equation (2) for first-order reaction; C = Dave and Chopra method [eqn. (3)].

plexes obtained from eqn. (1) differed from those obtained using eqns. (2) and (3).

REFERENCES

1 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
2 N.G. Dave and S.K. Chopra, Z. Phys. Chem., 48 (1966) 257.
3 G. Marcotrigiano and G.C. Pellacani, Z. Anorg. Allg. Chem., 413 (2) (1975) 171.
4 H.H. Horowitz and G. Metzer, Anal. Chem., 35 (1963) 1464.