Thermochimica Acta, 56 (1982) 217–219
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF SOME METAL HIPPURATES FROM DTG CURVES

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(Received 5 January 1982)

Sawhney and Bains [1] studied the non-isothermal decomposition of metal complexes of hippuric acid with Cu(II), Cd(II), Pb(II), and Fe(III). Sawhney and Matta [2] and Matta [3] probed kinetically the desolvation of cerium(III), neodynium(III) and erbium(III)–hippuric acid complexes. This note describes the kinetics of the pyrolytic dissociation of anhydrous complexes of hippuric acid with Ce(III), Nd(III) and Er(III) and solvated silver hippurate using Dave–Chopra eqns. (1) and (2)

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

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

where the terms have their usual meaning [4].

EXPERIMENTAL

All the reagents used were of analytical grade. The metal derivatives were isolated by the slow addition of sodium hippurate to the metal solution. The precipitate was digested over a water bath for 1 h, allowed to stand, filtered, washed, and dried at 35–40°C. Analytical data were in agreement with the composition given by Matta [3]. For solvated silver hippurate, elemental analysis suggested the composition: $C_6H_5CONHCH_2COOAG \cdot 1.5\ H_2O$:

	C%	H%	Ag%
Found	34.51	2.56	35.64
Calcd.	35.07	3.31	34.51

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Air-dried metal hippurates were pyrolysed on a manually operated assembly equipped with a Toshiniwal furnace at a rate of 6°C min^{-1} [Ce(III), Nd(III) and Er(III) complexes] and 10°C min^{-1} (silver hippurate).

RESULTS AND DISCUSSION

All the reactions under investigation follow the type of reaction [5]

$$A(s) \rightarrow B(s) + C(g)$$

Each sigmoidal trace in the pyrolysis curves was separately analyzed kinetically. The pyrolysis curves of the metal complexes, except solvated silver hippurate which showed three sigmoidal traces:

	% Loss	
	Found	Calcd.
(1) Ag R·1.5 $H_2O \rightarrow$ Ag R+1.5 H_2O	9.41	8.63
(2) Ag R $\rightarrow$ Ag 1/8R+7/8R	58.42	58.39
(3) Ag 1/8R $\rightarrow$ Ag+1/8R	64.36	65.50

R=$C_6H_5CONH\ CH_2COO$

were explained by Sawhney and Matta [2].

TABLE 1

Kinetic parameters for the non-isothermal decomposition of metal hippurates

Reaction	Temp. range (°C)	Eqn. (2)			Eqn. (1)	
		n	*E* (kcal mole^{-1})	*Z*	*n*	*E* (kcal mole^{-1})
Er $R_3 \rightarrow$ Er 1.5 R+1.5 R	240–440	1	11.44	0.21	0.67	16.02
Er 1.5 R $\rightarrow$ Metal oxide+ volatile product	480–600	1	19.87	0.14	0.63	45.70
Nd $R_3 \rightarrow$ Metal oxide+ volatile product	265–640	1	7.45	0.14	0.64	7.31
Ce $R_3 \rightarrow$ Metal oxide+ volatile product	227–520	1	7.95	0.12	0.68	9.13
Ag R·1.5 $H_2O \rightarrow$ Ag R+ 1.5 H_2O	60–180	1	12.42	1.74	0.80	25.42
Ag R $\rightarrow$ Ag 1/8 R+7/8 R	220–460	1	8.94	0.30	0.70	11.43
Ag 1/8 R $\rightarrow$ Ag+1/8 R	250–600	1	19.87	0.29		

R=$C_6H_5CONHCH_2COO$ (hippurate ion).

The total area (A) and area (a) at time t under the DTG curves corresponding to different temperatures were calculated with a planimeter. A plot of $T^{-1}/\log(A-a)$ vs. $\log(dx/dt)/\log(A-a)$ [eqn. (1)] for the reactions under study gave a straight line of slope $-E/2.303\ R$ and intercept n. The Kinetic parameters for the reactions were also estimated by presuming $n=1$ and using [eqn. (2)]. A straight line relationship followed on plotting $\log k$ vs. the reciprocal of absolute temperature; this indicates that desolvation/decomposition follows first order kinetics. The activation energy (E) and frequency factor (Z) were obtained from the slope, $-E/2.303\ R$, and the intercept of the straight line ($\log Z$), respectively.

Table 1 gives the values of the kinetic parameters for the non-isothermal desolvation/decomposition of metal hippurates. Analysis of the data shows that the decomposition/desolvation reaction under study with abnormally low Z values is a slow process.

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