Thermochimica Acta, 115 (1987) 381–384
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

PYROLYSIS AND KINETICS OF NON-ISOTHERMAL DECOMPOSITION OF La(III)- AND Th(IV)-PHENOXYMETHYL PENICILLIN COMPLEXES

S.S. SAWHNEY, D.N. DANGWAL and GAMBHIR SINGH CHAUHAN
Chemistry Department, D.A.V. (P.G.) College, Dehra Dun 248 001 (India)

(Received 10 September 1986)

The large role of penicillins is well documented. Recent researchers have incriminated mixed metal complexes involving penicillins, metals and some proteins in the human body for body abnormalities. Sawhney et al. [1–4] have investigated the formation of the complex species comprising metal and penicillins in solution. This report concerns the thermal decomposition mechanism and rate-determining steps of the metal complexes of phenoxymethyl penicillin with La(III) and Th(IV).

EXPERIMENTAL

All the chemicals used were of analytical grade. For isolation of the complexes in the solid state, an aqueous solution of the metal salt was added slowly and with constant stirring to the aqueous solution of phenoxymethyl penicillin (sodium salt). The precipitate was filtered, washed with ice-cold water and dried at 35–40 ° C.

The solid metal complexes were pyrolysed on a manually operated assembly equipped with a Toshniwal balance at a rate of 10 ° C min^{-1}.

RESULTS AND DISCUSSION

Pyrolysis tracings for La(III)- and Th(IV)-phenoxymethyl penicillin complexes displayed three and two sigmoids, respectively; the first sigmoid (40–140 and 60–140 ° C, respectively) showed the loss of three water molecules in the respective TG traces. From $LaR(NO_3)_2$ ($R = C_{16}H_{17}O_5N_2S$; 140–160 ° C), 17/25R departed at 160–360 ° C leaving $La \cdot 8/25R(NO_3)_2$, the weight of which remained constant in the temperature range 360–420 ° C; a further 8/25R escaped as gaseous materials (420–680 ° C) forming the final product (X) (constant weight at 680 ° C onwards), the composition of which could not be established. $ThR(NO_3) \cdot 3H_2O$ did not show any weight loss up to 60 ° C; the plateau at 140–160 ° C corresponds to $ThR(NO_3)_3$.

0040-6031/87/$03.50

TABLE 1

Kinetic data on nonisothermal decomposition of metal complexes of phenoxymethyl penicillin with La(III) and Th(IV)

Reaction [a]	Temp. range (°C)	n	E (kcal mol^{-1})	log Z (min^{-1})
$LaR(NO_3)_2 \cdot 3H_2O \rightarrow$ $LaR(NO_3)_2 + 3H_2O\uparrow$	40–140	1	3.48	−1.45
$LaR(NO_3)_2 \rightarrow$ $La \cdot 8/25R(NO_3)_2 + 17/25R\uparrow$	160–360	1	10.68	−2.00
$La \cdot 8/25R(NO_3)_2 \rightarrow$ $X + 8/25R\uparrow$	420–680	1	4.69	−2.25
$ThR(NO_3)_3 \cdot 3H_2O \rightarrow$ $ThR(NO_3)_3 + 3H_2O\uparrow$	60–140	1	10.98	−1.15
$ThR(NO_3)_3 \rightarrow$ $ThO_2 + DP\uparrow$	160–560	1	6.10	−2.60

[a] DP = dissociation product.

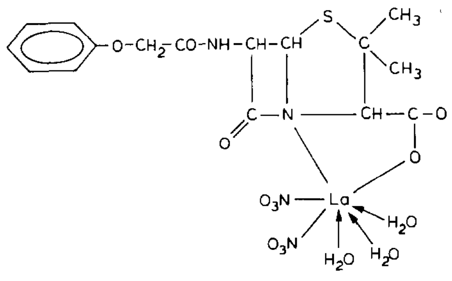
Further cleavage began at 160 °C and was complete at 560 °C, after which the constant weight tallied with ThO_2. Table 1 gives the pyrolysis and analytical data.

TABLE 2

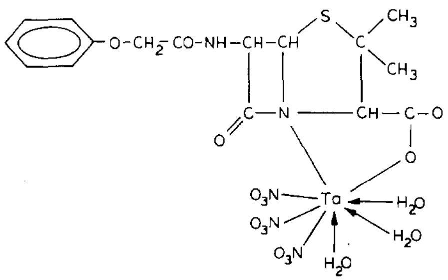
Pyrolysis data

Constant weight phases and (temp. range) (°C)	Loss (%) Found		Calc.
$LaR(NO_3)_2 \cdot 3H_2O$ (up to 40)			
$LaR(NO_3)_2$ (140–160)	8.14	$(3H_2O)$ [a]	8.11
$La \cdot 8/25R(NO_3)_2$ (360–420)	56.87	(17/25R) [a]	57.02
X (680 onwards)	37.39	(8/25R) [a]	38.78
$ThR(NO_3)_3 \cdot 3H_2O$ (up to 60)			
$ThR(NO_3)_3$ (140–160)	7.69	$(3H_2O)$ [a]	6.58
ThO_2 (560 onwards)	67.67	$[R(NO_3)_3]$ [a]	68.45

[a] Split off parts of the complexes.



Scheme 1. La(III)–phenoxymethyl penicillin complex.



Scheme 2. Th(IV)–phenoxymethyl penicillin complex.

Each sigmoid was analysed to estimate the kinetic parameters of the non-isothermal decomposition of the complexes using the Dave and Chopra equation for first-order reactions [5]:

$$k = \frac{\mathrm{d}x/\mathrm{d}t}{A - a} \qquad \text{when } n = 1$$

where A is the total area under the DTG curve and a stands for the area at time t. Values of log k were plotted against the reciprocal of the absolut temperature. The ensuing straight line relationship, justifying this equation yielded values for E and Z from its slope and intercept. All the reactions listed in Table 2 follow first-order kinetics. The very low values of Z indicate that the reactions are slow processes.

Activation energies of the reactions revealed that the phenoxymethyl penicillin is more strongly bound than water molecules to La(III); for the Th(IV)–phenoxymethyl penicillin complex, more energy is required to split off water molecules than for any other molecules from the parent compound. Table 2 gives the kinetic data.

The pyrolysis data suggested the structures given in Schemes 1 and 2 for the complexes under study.

REFERENCES

1 S.S. Sawhney and D.N. Dangwal, Thermochim. Acta, 77 (1984) 451.
2 S.S. Sawhney and D.N. Dangwal, Thermochim. Acta, 75 (1984) 259.
3 S.S. Sawhney and D.N. Dangwal, Thermochim. Acta, 67 (1983) 383.
4 S.S. Sawhney and A.K. Bansal, Thermochim. Acta, 60 (1983) 229.
5 N.G. Dave and S.K. Chopra, Z. Phys. Chem., 48 (1966) 257.