Thermochimica Acta, 62 (1983) 125–127
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

THERMOGRAVIMETRIC STUDY OF THE KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF METAL DERIVATIVES OF L-LYSINE MONOHYDROCHLORIDE

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(Received 13 August 1982)

L-Lysine monohydrochloride has been investigated as a ligand and has been found to form 1 : 3 and 1 : 2 chelates with arsenic and barium, respectively. A survey of the literature reveals that L-Lysine monohydrochloride as a ligand has not been studied systematically. Preliminary studies on the chelates of lysine with molybdenum [1], copper [2] and chromium [3] have been carried out. The present communication concerns the thermogravimetric study of metal chelates of L-lysine monohydrochloride with As(III) and Ba(II), with a view to probing kinetically the non-isothermal decomposition of the metal chelates following Dave and Chopra [4] expressions which are applicable, even under conditions where the factors known to be sensitive to kinetic data [5], remain inconsistent under experimental conditions.

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

where the terms have their usual meaning. If $n = 1$, eqn. (1) reduces to

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

EXPERIMENTAL

All the reagents were of BDH quality. For the synthesis of metal chelates, an aqueous solution of the ligand was slowly added to aqueous solutions of arsenic trichloride and barium chloride. The pH of the resulting mixture was raised to 8.0 by dropwise addition of NaOH solution. The mixture was warmed, allowed to stand overnight, and then concentrated over a water bath. The chelates precipitated on cooling, and were filtered, washed with

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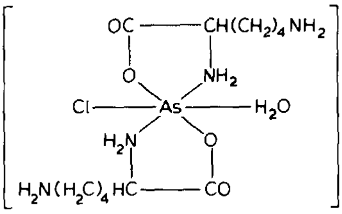
0040-6031/83/0000–0000/$03.00

ice-cold water and recrystallised from distilled water and finally dried in a vacuum desiccator over anhydrous calcium chloride. A tally of found and calculated values of elemental analysis for $As(C_6H_{13}O_2N_2)_2Cl \cdot H_2O$ and $Ba(C_6H_{13}O_2N_2)_2$ was observed. Samples were pyrolysed at the rate of 10°C min^{-1} manually utilising a modern thermogravimetric balance with a Toshniwal furnace in air.

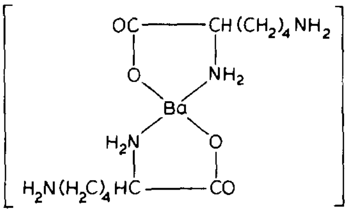
RESULTS AND DISCUSSION

Pyrolysis curves of the metal chelates showed only two sigmoidal traces. Having one H_2O molecule, arsenic lysinato chloride was stable up to 60°C, after which loss of the water molecule started and was completed at 140°C; a plateau (140–170°C) corresponding to arsenic lysinato chloride was observed. Organic matter was lost between 170 and 460°C, after which a plateau corresponding to As_2O_3 was observed. Lysinato barium was found to be stable up to 50°C, after which part of the organic matter was lost up to 240°C. A plateau (240–300°C) corresponding to $Ba(C_6H_{13}N_2O_2)_{16/19}$ was observed. Between 300 and 500°C the remaining organic matter was lost, after which a plateau showing BaO was observed.

Analytical data are shown in Table 1. The tentative structures of the chelates may be shown as



Central metal ligancy No=6



Central metal ligancy No=4

Each sigmoidal trace was analysed for kinetic study. Non-isothermal decomposition of the metal chelates under study resembles the reaction

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

which can be studied kinetically.

TABLE 1

Analytical data

Chelate	H_2O%		Oxide%	
	Found	Calcd.	Found	Calcd.
$(C_6H_{13}O_2N_2)_2AsCl \cdot H_2O$	3.08	3.60	42.59	40.22
$(C_6H_{13}O_2N_2)_2Ba$			27.39	30.38

TABLE 2

Kinetic data

Reaction	E (kcal mole^{-1})	log Z
$(C_6H_{13}O_2N_2)_2AsCl \cdot H_2O \rightarrow$ $(C_6H_{13}O_2N_2)_2AsCl + H_2O$	12.58	0.85
$(C_6H_{13}O_2N_2)_2AsCl \rightarrow As_2O_3$ + dissocn. product	11.44	0.62
$(C_6H_{13}O_2N_2)_2Ba \rightarrow$ $(C_6H_{13}O_2N_2)_{19/25}Ba$ + dissocn. product	10.30	0.23
$(C_6H_{13}O_2N_2)_{19/25}Ba \rightarrow BaO$ + dissocn. product	21.74	0.325

From DTG curves, A, a, and dx/dt were calculated; k values corresponding to different temperatures were computed using eqn. (1) for first order kinetics. A straight line relationship on plotting log k vs. T^{-1} indicates that the non-isothermal decomposition/desolvation follows first order kinetics. The slope and intercept gave the values of E and Z (collision number), respectively. The reactions under study appear to be slow processes as log Z values appear to be abnormally low. Table 2 contains kinetic data.

With a manually operated assembly as used in the present study, kinetic data computed using Dave and Chopra's method are quite dependable even if factors such as heating rate, temperature variance, etc., which contribute significantly if slope dependent procedures [6,7] are employed, could not be kept reasonably constant.

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