Note

TG STUDY OF THE KINETICS OF PYROLYTIC DECOMPOSITION OF COMPLEXES OF L-LYSINE MONOHYDROCHLORIDE

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L-Lysine monohydrochloride has been found to form $1:2$ complexes with Zn(II), Hg(II) and Cd(II) at pH 8–9 [1]. Sharma and others have studied the metal complexes of amino acids to be found in the biological and pharmaceutical fields [2–5]. The present communication concerns the thermogravimetric study of metal complexes of L-lysine monohydrochloride using the Dave and Chopra [6] expression which is applicable even when the factors known to be sensitive to the kinetic data [7] remain inconsistent under the 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 meanings, if $n = 1$, eqn. (1) reduces to

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

EXPERIMENTAL

All reagents used were of BDH AnalaR quality. For the syntheses of the metal complexes, aqueous solutions of aluminium trichloride and cobalt chloride were used. The pH of the resulting mixture was raised to 9 by the dropwise addition of NaOH solution. The mixture was warmed, allowed to stand overnight and then concentrated over a water bath. The complexes which precipitated on cooling were filtered, washed with ice-cold water, recrystallised from distilled water and finally dried in a vacuum desiccator over anhydrous calcium chloride. A set of found and calculated values of the elemental analyses of $Al(L_2 \cdot 2H_2O) \cdot 4H_2O$ and $Co(L_2 \cdot 2H_2O) \cdot 4H_2O$ was compared. Samples were pyrolysed at a 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 derivatives showed three sigmoidal traces for aluminium and cobalt lysinato hexahydrates, which were found to be stable up to 65°C. Loss of water of crystallisation then began, which was complete at 95°C, after which a plateau (95–105°C) corresponding to aluminium lysinato dihydrate was seen. Between 105 and 128°C two molecules of water were lost, after which a plateau at 125–176°C was obtained corresponding to aluminium lysinate. The decomposition of organic matter started at 176°C and was complete at 480°C, when a plateau corresponding to Al_2O_3 was again obtained. L-Lysinato cobalt hexahydrate was stable up to 700°C. The loss of water of crystallisation was observed between 79 and 98°C when a plateau (98–110°C) corresponding to lysinato cobalt dihydrate was obtained. The loss of coordinated water occurred between 110 and 135°C. Again a plateau at 135–225°C was seen corresponding to the lysinato cobalt complex. The loss of organic matter began at 225°C and was complete at 530°C when a plateau corresponding to cobalt oxide appeared.

Analytical data for the compounds under study are shown in Table 1. Tentative structures of the chelates are shown in Fig. 1.

For the kinetic study, each sigmoidal trace was analysed. The non-isothermal decomposition of the metal derivatives under study resembles the reaction

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$
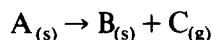
From the DTG curves, A, a and dx/dt were calculated and K values corresponding to different temperatures were computed using eqn. (1) for first-order kinetics. The straight-line relationship formed on plotting $\log K$ vs. T^{-1} indicates that the non-isothermal decomposition follows first-order kinetics. The slope and intercept give the values of E and Z (collision number). The reactions under study appear to be slow processes, since $\log Z$ values are very low. Table 2 contains kinetic data for the reactions under study. With the manually operated assembly used in the present study,

TABLE 1

Analytical data for the compounds under study

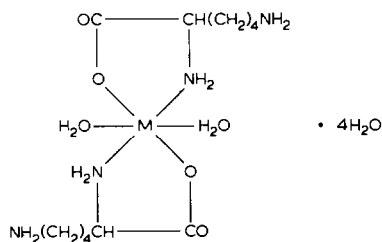|	Theoretical data	Calculated data
$AlL_2 \cdot 6H_2O$		
% metal oxide	20.4	20.1
% water molecules	23.06	22.5
$CoL_2 \cdot 6H_2O$		
% metal oxide	16.4	16.3
% water molecules	23.6	23.2

Fig. 1. Tentative structures of the chelates. M = Al(III), Co(III).

TABLE 2

Kinetic data for the reactions under study

Molecular formula	E	Log Z
$AlL_2 \cdot 6H_2O$	14.56	0.56
	12.62	0.52
	10.80	0.46
$CoL_2 \cdot 6H_2O$	18.00	0.76
	15.56	0.68
	12.60	0.54

kinetic data computed with the Dave–Chopra method [6] are quite reliable even if the factors, i.e., heating rate, temperature variance, etc., which contribute significantly if slope-dependent procedures [7,8] are employed, could not be kept reasonably constant.

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