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Note

EVALUATION OF THE KINETICS OF PYROLYTIC DECOMPOSITION OF METAL DERIVATIVES OF L-LYSINE MONOHYDROCHLORIDE FROM DTG CURVES

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L-Lysine monohydrochloride has been investigated as a ligand and it has been found that it forms 1 : 3 and 1 : 2 chelates with arsenic and barium, respectively. The authors [1] have investigated the kinetics of non-isothermal decomposition of some metal complexes of L-lysine monohydrochloride using the Dave–Chopra method [2]. The present communication concerns the estimation of the kinetic parameters of the pyrolytic decomposition of some metal complexes of L-lysine monohydrochloride with Pr(III), Nd(II) and Cr(III), using Dave–Chopra expressions which are applicable even under conditions where the factors, known to be sensitive to kinetic data [3], 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 meanings. When $n = 1$, eqn. (1) reduces to

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

EXPERIMENTAL

All the reagents used were of B.D.H. Analar quality. For synthesis of the metal derivatives, an aqueous solution of the ligand was added slowly to aqueous solutions of Pr(III), Nd(II) and Cr(III) chlorides. 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. On cooling, the derivatives were precipitated out of solution. The precipitates were filtered, washed with ice-cold water, recrystal-

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lised from distilled water and, finally, dried in a vacuum desiccator over anhydrous calcium chloride. Experimental and calculated values of elemental analysis for $(C_6H_{13}O_2N_2)_2Pr \cdot 2\ H_2O$, $(C_6H_{13}O_2N_2)_2Nd \cdot 2\ H_2O$ and $(C_6H_{13}O_2N_2)_2Cr \cdot 2\ H_2O$ were compared. The samples were pyrolysed in air at a rate of 10°C min^{-1} with manual operation of a modern thermogravimetric balance equipped with a Toshniwal furnace.

RESULTS AND DISCUSSION

Pyrolysis curves of metal derivatives showed only two sigmoidal traces. Lysinato praseodymium dihydrate was stable up to 82°C, after which loss of water molecules was initiated, being complete at 135°C; a plateau (135–190°C) corresponding to lysinato praseodymium was observed. Between 190 and 540°C, organic matter was lost after which a plateau corresponding to Pr_2O_3 was observed. Lysinato neodymium dihydrate was found to be stable up to 45°C, after which loss of water molecules was initiated, being complete at 90°C; a plateau (90–175°C) corresponding to lysinato neodymium was observed. Between 175 and 360°C organic matter was lost quickly, after which slow decomposition up to 480°C was observed: above 480°C a plateau corresponding to Nd_2O_3 was noticed. Lysinato chromium dihydrate is stable up to 70°C and then loses water molecules up to 110°C; between 110 and 170°C a constant weight corresponding to lysinato chromium was observed. Organic matter was lost between 170 and 430°C, after which a plateau, corresponding to Cr_2O_3 appeared.

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

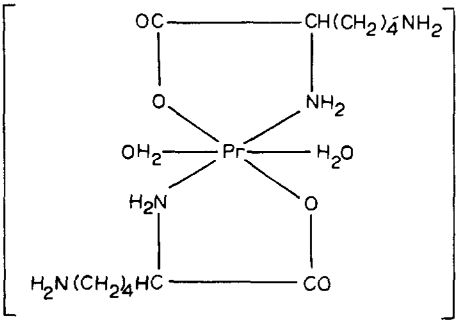
For kinetic study, each sigmoidal trace was analysed. Non-isothermal decomposition of the metal derivatives under study resembles the reaction $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$, which can be studied kinetically.

From the DTG curves A, a and dx/dt were calculated; k values corresponding to different temperatures were computed, using eqn. (1) for first-

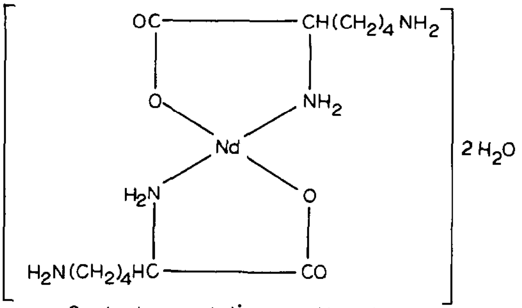
TABLE 1

Analytical data

Derivative	H_2O		Oxide	
	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)
$(C_6H_{13}O_2N_2)_2Pr \cdot 2\ H_2O$	8.02	7.72	38.5	35.21
$(C_6H_{13}O_2N_2)_2Nd \cdot 2\ H_2O$	7.92	7.65	37.02	35.45
$(C_6H_{13}O_2N_2)_2Cr \cdot 2\ H_2O$	10.58	9.52	21.05	20.11



Central metal ligancy No. =6



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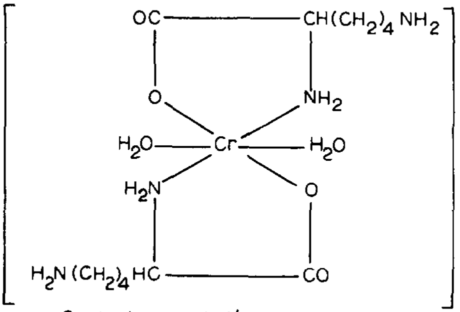

Central metal ligancy No. = 6

Fig. 1. Tentative structures of the metal derivatives.

order kinetics. A straight-line relationship formed on plotting log k vs. T^{-1}, indicates that the non-isothermal decomposition follow first-order kinetics. The slope and intercept gave the values of E and z (collision number). The reactions under study appear to be slow processes as log z values are very low. Table 2 contains the kinetic data, for the reactions under study. With the manually-operated assembly used in the present study kinetic data computed with the Dave–Chopra method are quite reliable even if the factors, i.e. heating rate, temperature variance, etc., which contributed significantly if the slope-dependent procedures [4,5] are employed, could not be reasonably kept constant.

TABLE 2

Kinetic data

Reaction [a]	E (kcal mole^{-1})	log z
$(C_6H_{13}O_2N_2)_2Pr \cdot 2\ H_2O \rightarrow (C_6H_{13}O_2N_2)_2Pr + 2\ H_2O$	15.60	0.76
$(C_6H_{13}O_2N_2)_2Pr \rightarrow Pr_2O_3 + d.p.$	10.56	0.68
$(C_6H_{13}O_2N_2)_2Nd \cdot 2\ H_2O \rightarrow (C_6H_{13}O_2N_2)_2Nd + 2\ H_2O$	16.88	0.82
$(C_6H_{13}O_2N_2)_2Nd \rightarrow Nd_2O_3 + d.p.$	12.30	0.56
$(C_6H_{13}O_2N_2)_2Cr \cdot 2\ H_2O \rightarrow (C_6H_{13}O_2N_2)_2Cr + 2\ H_2O$	10.28	0.46
$(C_6H_{13}O_2N_2)_2Cr \rightarrow Cr_2O_3 + d.p.$	18.76	0.36

[a] d.p. = dissociation product.

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