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A Study of Non-Isothermal Decomposition of Calcium *dl*-Lactate Pentahydrate

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The thermal decomposition of calcium *dl*-lactate pentahydrate has been studied under non-isothermal conditions in static air atmosphere with heating rate programmed at $\frac{1}{6}$ Ks^{-1}. The thermogravimetric data thus obtained have been analysed for the kinetic parameters of the two decomposition steps using Freeman-Carrol, Horowitz-Metzer, Coats Redfern, Fuoss, Karkhanawala-Dharwadkar and Zsako methods. Decomposition mechanisms have also been suggested.

INTRODUCTION

Calcium tartarate has been reported to furnish calcium carbonate above 703 K till 1023 K making it useful for accurate automatic determination[1] of calcium and tartarate ions. Salts and complexes of alkaline earth metals and rare earths have assumed much importance in the study of intermediates of their thermal decomposition on account of interesting conductivity related properties of some of the latter. It was therefore, considered worthwhile to study the thermal decomposition of calcium *dl*-lactate pentahydrate which has escaped attention of workers till now and to find out the kinetic parameters of the decomposition steps which could explain the mechanism of decomposition.

EXPERIMENTAL

The lactate was synthesized by the usual method[2] of addition of calcium carbonate to lactic acid (sp gr. 1.195, BDH) till appearance of a slight turbidity. The solution was filtered. The filtrate was evaporated on a water-bath to a small volume and the lactate was allowed to crystallize. The salt was recrystallized from water and dried in vacuum desiccator over anhydrous calcium chloride. It was analysed for $Ca(CH_3CHOH\ COO)_2 5H_2O$. Calcium was estimated gravimetrically as calcium carbonate[3] and the percentage of carbon and hydrogen was found out by Duma method.

The IR spectra of the compound and residue obtained upon heating were recorded in nujoll mull on the range of 4000–200 cm^{-1} on Perkin-Elmer IR spectrophotometer. The thermogravimetric analysis was carried out on Stanton-

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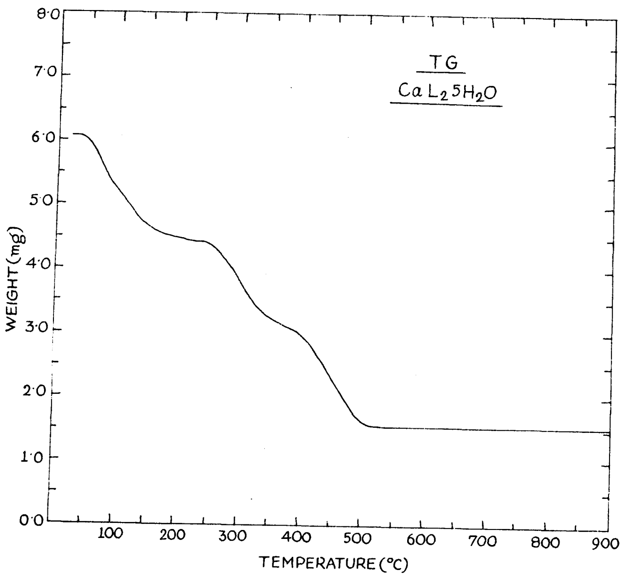

Fig. 1 TG Trace of calcium *dl*-lactate pentahydrate.

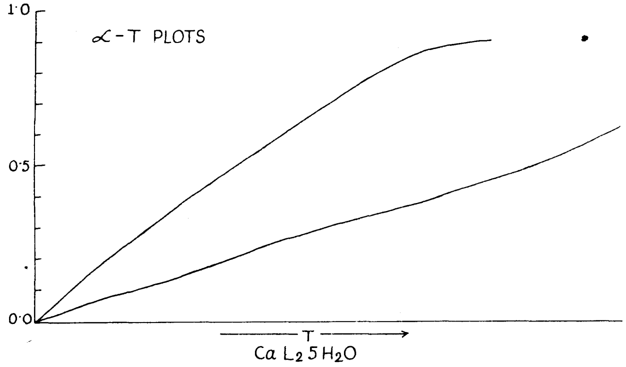

Fig. 2 α–*T* plots of the two steps of thermal decomposition of calcium *dl*-lactate pentahydrate.

Redcroft Thermobalance TG 750 connected with a recorder operating on 0.1 mV full scale. Temperature versus weight curve was obtained. The sample was powdered in order to increase surface area and allow good exchange of material. The powder was loosely poured into the sample holder and dispersed as well as possible in order to counteract the poor thermal conductivity. These steps were taken to minimise the disturbing influence of local factors and bring reproducibility. The TG trace was recorded after keeping the freshly prepared crystals in desiccator for eight days.

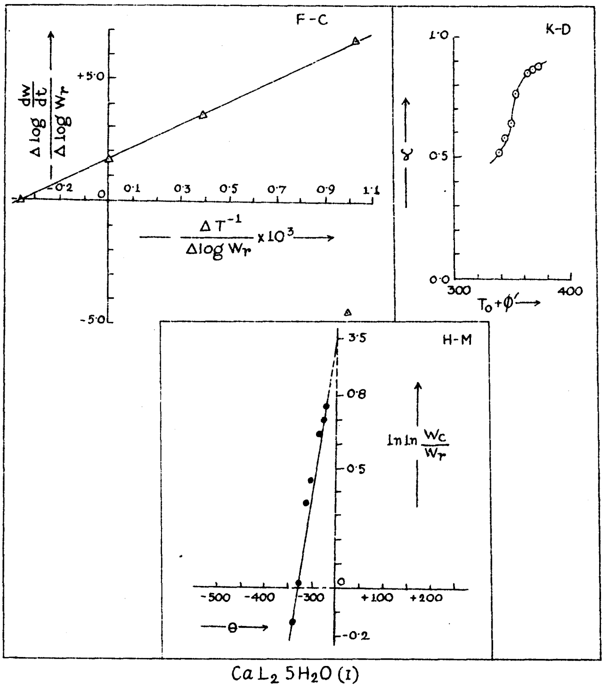

Fig. 3 Freeman-Carroll, Karkhanawala-Dharwadkar and Horowitz-Metzger plots of the first step of decomposition of calcium *dl*-lactate pentahydrate.

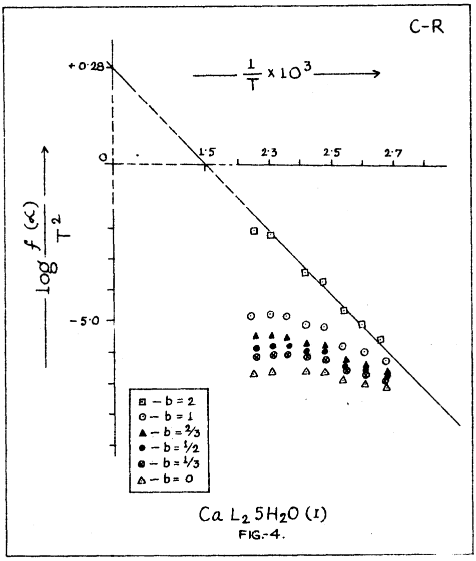

Fig. 4 The most linear Coats-Redfern plot for the first step of decomposition of calcium *dl*-lactate pentahydrate.

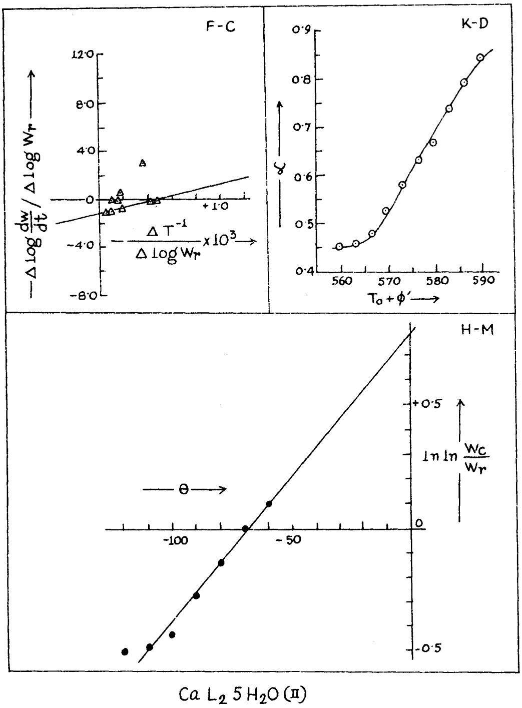

Fig. 5 Freeman-Carroll, Karkhanawala-Dharwadkar and Horowitz-Metzger plots of the second step of decomposition of calcium *dl*-lactate pentahydrate.

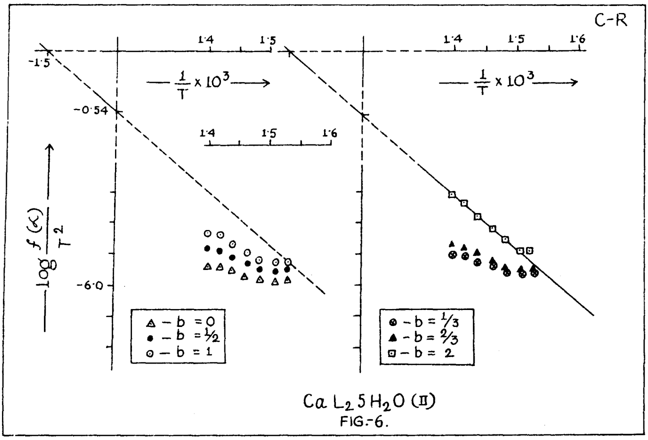

Fig. 6 The most linear Coats-Redfern plot for the second step of decomposition of calcium *dl*-lactate pentahydrate.

RESULTS AND DISCUSSION

The IR bands appearing at 3290 cm^{-1} and 1607 cm^{-1} in the compound disappears completely in the first step of heating confirming dehydration of the compound. This step begins at 303 K and is slow initially but soon the loss becomes precipitous and the step slowly ends at 503 K. The anhydrous salt is stable only up to 513 K when it starts loosing weight again till 813 K when the residue corresponds to calcium oxide.

The (α–T) plots do not show any induction period in any of the two steps suggesting[4] that the initial stages involved little or no physical desorption. This also indicates that no surface nucleation or branching occurs before the decomposition starts. The (α–T) plots begin with apparent accelaratory period followed by region of maximum rate. This suggests that there is no significant decay or retention period like those observed in the case of some succinates[5].

The TG data on the steps which were thus identified as follows were analysed using the different differential methods of Freeman-Carroll[6], Horowitz-Metzger[7], Coats-Redfern[8], Fuoss[9] *et. al.*, Karkhanawala-Dharwadkar[10] and Zsako[11] methods (equations 1 to 5).

Step I [303–503 K]:

$$Ca(CH_3CHOH\ COO)_2 5H_2O \longrightarrow Ca(CH_3CHOH\ COO)_2$$

Step II [513–813 K]: $Ca(CH_3CHOH\ COO)_2 \longrightarrow CaO$

F–C:
$$-\frac{\frac{E}{2.303R}\Delta T^{-1}}{\Delta \log W_r} = -b + \frac{\Delta \log dw/dt}{\Delta \log W_r} \qquad (1)$$

H–M:
$$\ln \ln \frac{W_c}{W_r} = \frac{E\theta}{RT_s^2} \qquad (2)$$

C–R:
$$\log \frac{F(\alpha)}{T^2} = \log \frac{ZR}{qE} - \frac{E}{4.575}\frac{1}{T} \qquad (3)$$

Fuoss/K–D:
$$E = -\left(\frac{RT_i^2}{w_i}\right)\left(\frac{dW}{dT}\right)_i \qquad (4)$$

Zsako:
$$\log \frac{ZE}{Rq} = \log g(\alpha) - \log p(x) - B \qquad (5)$$

where E = activation energy, Z = collision frequency, b=order of reaction, $W_r = W_c - W$, W_c = weight loss at completion of reaction, W= total weight loss up to time t, R = gas constant, T = absolute temperature, T_s = reference temperature such that at $T_S = \frac{|W|}{W_0} = \frac{1}{c}$, $\theta = T - T_S$, α = conversion degree, $F(\alpha)$ = conversion integral, q = heating rate, T_i = temperature of inflexion, W_i = weight at T_i and $\left(\frac{dw}{dT}\right)_i$ = slope at the point of inflexion.

TABLE 1
VALUES OF KINETIC PARAMETERS OF THE TWO STEPS OF THERMAL DECOMPOSITION OF CALCIUM *dl*-LACTATE PENTAHYDRATE

Step	Kinetic parameters	F–C	H–W	C–R	Fuoss	F–D	Zsako
I	E(KJ mol^{-1})	92.445	96.190	35.731	34.317	37.668	33.890
	Z(S^{-1})	8.799×10^{11}	3.283×10^{4}	1.365×10^{3}	9.84×10^{2}	2.271×10^{3}	3.087×10^{2}
	$\Delta S^{\neq}$(Jκ · mol^{-1})	−18.115	−160.349	−186.789	−189.817	−182.562	−199.921
	b	1.69	1/3	2	—	—	2
II	E(KJ mol^{-1})	56.061	58.367	68.910	78.488	61.362	37.656
	Z(S^{-1})	1.265×10^{3}	0.17×10^{2}	4.79×10^{3}	4.985×10^{4}	1.72×10^{3}	7.342×10^{2}
	$\Delta S^{\neq}$(Jk^{-1} mol^{-1})	−192.39	−228.235	−181.318	−161.845	−189.842	−196.921
	b	1.2	1/2	2	—	—	2

The values of order of reaction, activation energy, collision frequency and activation entropy for the two steps as obtained by different method have been given in Table 1.

The values of activation entropy of both the steps suggest appreciable rearrangement among various degrees of freedom leading to more ordered structure of transition state.

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