NON-ISOTHERMAL DEHYDRATION AND DECOMPOSITION OF *dl*-LACTATES OF TRANSITION METALS AND ALKALINE EARTH METALS
A comparative study

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A comparative study of the non-isothermal decomposition of the *dl*-lactate hydrates of magnesium, calcium and strontium has been made with that of the *dl*-lactate hydrates chromium(III), manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) keeping dry air as the purge gas and the heating rate maintained at 10 K min^{-1}. While the *dl*-lactates of manganese(II), cobalt(II) and copper(II) followed single step decomposition scheme suggesting that dehydration and decomposition steps overlapped, the dehydration steps of the other compounds were distinct. α–T plots of none of the dehydration steps showed any induction period, indicating no physical desorption, nucleation or branching. Neither the α_{max}-values nor the onset temperatures of the dehydration steps did show any pattern. The TG data of the dehydration steps have also been analyzed using the Freeman–Carroll, Horowitz–Metzger, Coats–Redfern, Zsakó, Fuoss–Salyer–Wilson and Karkhanavala–Dharwadkar methods. Values of order of reaction, activation energy and Arrhenius factor have been approximated and compared. There are similarities in the activation energy values for the dehydration steps (< 60 kJ mol^{-1} in general). It is higher with group 2 metals and lower in transition metals (maximum in magnesium and lowest in chromium and iron lactates). In cases of overlapping of dehydration and decomposition steps, the activation energy values are on the lower side with the same trend (lower in cobalt and copper cases).

Keywords: activation energy, kinetic studies, metal lactates, non-isothermal dehydration

Introduction

Thermal decompositions of hydrated carboxylates have been attracting thermal analysts [1–14] either for testing the efficacy of a procedure or for preparation of a new material or for searching 'meaningful data' on the thermal dehydrations and decompositions. Salts of hydroxyl acids have also aroused interest [9]. Lactic acid is an important constituent of many food stuffs which are frequently subjected to heating and the significance of most of the first transition series metals as important trace metals and that of the group 2 metals aroused interest in taking up a systematic study of thermal decomposition of *dl*-lactates of those metals, in the present work. The onset temperatures of dehydrations have recently been searched for any sequence among the salts of the aliphatic series of carboxylates [2]. Like most organic salts the *dl*-lactate hydrates of chromium(III), iron(II), nickel(II) and zinc(II) have been found to be undergoing two-step decomposition involving dehydration and decomposition to respective oxides at moderate rates of heating in air while the *dl*-lactates of manganese(II), cobalt(II) and copper(II), however, have been found to be undergoing single step decomposition scheme indicating that the two processes overlap.

Experimental

Materials and methods

The hydrates of *dl*-lactates of magnesium, calcium, strontium, chromium(III), manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) were synthesized by the usual method [16] of addition of respective metal carbonates to lactic acid [sp.gr.1.95] till a slight turbidity appeared. The solution was filtered. The filtrate was evaporated on a water bath to a small volume and the lactate was allowed to crystallize. The carboxylates were recrystallised from water and dried in vacuo over anhydrous calcium chloride and analysed to confirm their stoichiometry. IR spectra of the freshly prepared samples were also recorded for confirming their identity on a Perkin Elmer Spectrophotometer 577 over a range of 4000–200 cm^{-1} using KBr-supporting disc.

The crushed lactate was loosely poured in each case, into the sample holder of Stanton-Redcroft TG 750 Thermobalance, and dispersed well. Minimising the local factors (besides using freshly prepared sample, precaution of keeping small sample size of 4–8 mg was also taken to minimize the impact of heat and mass transfer phenomena), the TG curves of all the *dl*-lactate hydrates were recorded using dry air as the purge gas with heat-

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ing rate programmed at 10 K min^{-1}. The residues were again analysed for the percentage of metals by dissolving them as usual.

Results and discussion

Like most organic salts [17], the *dl*-lactates of magnesium, chromium(III), iron(II), nickel(II) and zinc(II) [6, 9] undergo two-step decomposition involving dehydration and decomposition to respective oxides (Table 2). The smoothness of the TG curves and the agreement between the calculated and observed mass loss suggest that dehydrations proceeded without any intermediates. The *dl*-lactates of calcium, strontium, manganese(II), cobalt(II) and copper(II), however, followed single step decomposition scheme indicating that the two processes overlap. The final decomposition products were also confirmed by estimating the percentage of the respective metals.

The α–T plots obtained from the TG data of none of the purely dehydration steps and the decomposition steps of the magnesium, calcium, strontium, cobalt(II) and zinc(II) compounds show any induction period indicating no physical desorption, nucleation or branching while the α–T plots of the other decomposition phenomena show a period of induction thus indicating that physical desorption and nucleation are taking place [18]. They were tested for the possible mechanistic models using the usual equations. The initial indications were supported to a great extent and they were

found to be following either an *n*th order kinetic path or an Avrami–Erofeev equation (Table 1).

The kinetics of the dehydration processes were analysed by means of the following popular methods and equations (Eqs (1)–(7)):

Freeman–Carroll [19]:

$$(E/2.303R)\Delta T^{-1}/\Delta \log w_r =$$
$$= -n + [\Delta \log(\mathrm{d}w/\mathrm{d}t)]/\Delta \log w_r \qquad (1)$$

Horowitz–Metzger [20]:

$$\ln \ln(w_c/w_r) = E\theta/RT_s^2 \qquad (2)$$

Coats–Redfern [21]: for $n=1$:

$$\log\{[\tilde{1}\log(-\alpha)/T^2]\} =$$
$$= [\log(AR/bE)](1-2RT/E) - E/2.303RT \qquad (3)$$

and for $n \neq 1$:

$$\log[1-(1-\alpha)^{1-n}][1/T^2(1-n)] =$$
$$= [\log(AR/bE)](1-2RT/E) - E/2.303RT \qquad (4)$$

Fuoss–Salyer–Wilson/Karkhanavala–Dharwadkar [22, 23]:

$$E = (RT_i^2/W_i)(\mathrm{d}W/\mathrm{d}T)_i \qquad (5)$$

Zsakó [24]:

$$\log(AE/Rb) = \log g(\alpha) - \log p(x) = B \qquad (6)$$

$$\log A = B + \log Rb - \log E \qquad (7)$$

where n is the order of reaction, w_r stands for the difference (w_c-w), w_c is the mass loss at completion of reaction (W_0-W_∞), w is that up to time t, T the absolute

Table 1 Comparative chart of the decomposition steps of *dl*-lactate hydrates and models followed

S. No.	Compounds	Temperature range/K	Suggested mode of decomposition	Model followed
1	$MgL_2 \cdot 6H_2O$	(i) 313–493 (ii) 503–533 (iii) 543–753	$MgL_2 \cdot 6H_2O \rightarrow MgL_2 \cdot 0.25H_2O$ $MgL_2 \cdot 0.25H_2O \rightarrow MgL_2$ $MgL_2 \rightarrow MgO$	2nd order kinetic ($n=2$) 3D diffusion
2	$CaL_2 \cdot 5H_2O$	(i) 303–503 (ii) 513–815	$CaL_2 \cdot 5H_2O \rightarrow CaL_2$ $CaL_2 \rightarrow CaO \cdot 0.5CO_2$	Avrami–Erofeev ($n=1.5$)
3	$SrL_2 \cdot H_2O$	(i) 303–363 (ii) 373–823	$SrL_2 \cdot H_2O \rightarrow SrL_2$ $SrL_2 \rightarrow SrO \cdot 0.25CO_2$	2nd order kinetic Avrami–Erofeev ($n=1$)
4	$CrL_3 \cdot 3H_2O$	(i) 313–553 (ii) 583–773	$CrL_3 \cdot 3H_2O \rightarrow CrL_3$ $CrL_3 \rightarrow 1/2Cr_2O_3$	2nd order kinetic ($n=2$) 3D diffusion
5	$MnL_2 \cdot 3H_2O$	303–553	$MnL_2 \cdot 3H_2O \rightarrow MnO$	Avrami–Erofeev ($n=1.5$)
6	$FeL_2 \cdot 5H_2O$	(i) 318–573	$FeL_2 \cdot 5H_2O \rightarrow FeL_2$ $FeL_2 \rightarrow 1/2Fe_2O_3$	2nd order kinetic Avrami–Erofeev ($n=1$)
7	$CoL_2 \cdot 3H_2O$	303–513	$CoL_2 \cdot 3H_2O \rightarrow CoO$	Three half kinetic
8	$NiL_2 \cdot 3H_2O$	(i) 303–455 (ii) 483–643	$NiL_2 \cdot 3H_2O \rightarrow NiL_2$ $NiL_2 \rightarrow NiO$	2nd order kinetic Avrami–Erofeev ($n=3$)
9	$CuL_2 \cdot 2H_2O$	303–473	$CuL_2 \cdot 2H_2O \rightarrow CuO$	Avrami–Erofeev ($n=3$)
10	$ZnL_2 \cdot 3H_2O$	(i) 353–463 (ii) 473–813	$ZnL_2 \cdot 3H_2O \rightarrow ZnL_2$ $ZnL_2 \rightarrow ZnO$	2/3 order kinetic path 1st order kinetic model

temperature, T_s the reference temperature such that at T_s, $|W/W_0|=1/e$, θ the difference $(T-T_s)$, $(dW/dT)_i$ the slope at the point of inflexion, subscript i stands for the point of inflexion and B is the A.M. of the most consistent series of B-values as obtained from Eq. (6). The values of $p(x)$ were taken from the Zsakó chart (x depends upon T and E).

In the Freeman–Carroll method, the intercept of the linear plot on the $[\Delta\log(dw/dt)]/\Delta\log w_r$ axis furnishes the value of order of the reaction where the E-value was obtained from the slope ($E/2.303R$). The slope in Horowitz–Metzger method was (E/RT_s^2) and in the Coats–Redfern method, equations of different orders were searched for the most linear plot which furnished activation energy from its slope ($E/2.303R$). In the Fuoss–Salyer–Wilson method, the activation en-

ergy value was obtained from the point of inflexion in the TG trace. The K–D method involved a plot of α *vs.* $(T_0+\phi)$ where $\phi=[(T_0-T)/(T_0-T_\infty)]\cdot100$ which furnished the point of inflexion leading to the E-value from Eq. (5). In Zsakó method the most consistent series of B was searched out by the standard deviation method. The values of the order of reaction and the activation energy, which corresponded to the most consistent series of B, were accepted. The standard deviation values obtained using the Zsakó chart, were extrapolated [6] to arrive at a minimum to furnish more appropriate value of the standard deviation in each case and hence that of activation energy. The values of A were also obtained using the methods described above. The values of the kinetic parameters have been put in Table 2.

Table 2 Comparative chart of the kinetic parameters of thermal dehydration and dehydration–decomposition of *dl*-lactates as obtained by different methods

Composition	Step	Kinetic parameters	F–C	H–M	C–R	F–S–W	K–D	Zsakó
$MgL_2\cdot6H_2O$	dehydration I	E	63	99	51	53	65	48
		A	$8\cdot10^6$	$4\cdot10^6$	$2\cdot10^3$	$3\cdot10^4$	$8\cdot10^6$	$4\cdot10^4$
		n	1.62	1	1	–	–	2
$MgL_2\cdot6H_2O$	dehydration II	E	134	195	162	173	132	182
		A	$2\cdot10^{12}$	$6\cdot10^{12}$	$6\cdot10^{11}$	$6\cdot10^{15}$	$9\cdot10^9$	$1.5\cdot10^{16}$
		n	1.4	1/2	1/2	–	–	1/2
$CaL_2\cdot5H_2O$	dehydration	E	92	96	36	34	38	48
		A	$9\cdot10^{11}$	$3\cdot10^4$	$1.4\cdot10^3$	$1\cdot10^3$	$2\cdot10^4$	$3.87\cdot10^4$
		n	1.69	1/3	2	–	–	2
$SrL_2\cdot5H_2O$	dehydration	E	47	–	40	26	32	36
		A	$2\cdot10^6$	–	$1\cdot10^4$	$0.4\cdot10^2$	$0.6\cdot10^2$	$2\cdot10^5$
		n	0.74	–	1/2	–	–	0
$CrL_3\cdot3H_2O$ [9]	dehydration	E	48	30	26	17	23	18
		A	$2\cdot10^5$	$5\cdot10^7$	$3\cdot10^4$	$4\cdot10^3$	$3\cdot10^4$	$1\cdot10^5$
		n	1.9	1/3	2	–	–	2
$FeL_2\cdot5H_2O$ [9]	dehydration	E	29	35	26	27	29	24
		A	$1\cdot10^3$	$3\cdot10^3$	$6\cdot10^3$	$7\cdot10^4$	$1.3\cdot10^2$	$1\cdot10^5$
		n	2.05	2/3	2	–	–	2
$NiL_2\cdot3H_2O$ [9]	dehydration	E	48	33	36	36	34	33
		A	$3\cdot10^5$	$1\cdot10^7$	$9\cdot10^6$	$1\cdot10^3$	$4\cdot10^3$	$4\cdot10^4$
		n	0.25	2	2	–	–	2
$ZnL_2\cdot3H_2O$ [6, 9]	dehydration	E	50	70	67	46	46	53
		A	$7\cdot10^5$	$2.5\cdot10^2$	$5\cdot10^6$	$6\cdot10^3$	$3\cdot10^4$	$1.5\cdot10^4$
		n	1.25	1/3	1	–	–	0
$MnL_2\cdot3H_2O$ [9]	dehydration-cum-decomposition	E	27	65	24	23	24	24
		A	$1\cdot10^2$	$1\cdot10^3$	$4\cdot10^5$	$1\cdot10^2$	$2\cdot10^2$	$1\cdot10^3$
		n	2.85	1/3	2	–	–	2
$CoL_2\cdot3H_2O$ [9]	dehydration-cum-decomopsition	E	46	21	16	18	18	14
		A	$6\cdot10^4$	$1\cdot10^2$	$9\cdot10^5$	$5\cdot10^3$	$1.3\cdot10^2$	$3\cdot10^3$
		n	4.56	1/3	2	–	–	2
$CuL_2\cdot2H_2O$ [9]	dehydration-cum-decomposition	E	24	19	16	30	24	15
		A	$4\cdot10^2$	$1.3\cdot10^2$	$3\cdot10^6$	$4\cdot10^4$	$7\cdot10^2$	$2\cdot10^3$
		n	0.25	0.2	1/2	–	–	2
$ZnL_2\cdot3H_2O$ [6]	decomposition only	E	104	82	66	56	59	66
		A	$1\cdot10^{10}$	$1\cdot10^3$	$3\cdot10^3$	$4\cdot10^2$	$6\cdot10^3$	$1.3\cdot10^3$
		n	0.8	0.15	1	–	–	1

E is in kJ mol^{-1}, A in s^{-1}

The following conclusions are drawn from the study:

- The initial indications (α–T) were supported to a great extent and they were found to be following either an *n*th order kinetic path or an Avrami–Erofeev equation (except the case of second step dehydration of magnesium and decomposition of chromium).
- The onset temperature does not follow any pattern.
- The order is non zero in general. The values of E_a is <60 kJ mol^{-1}. Low for the overlapping cases!!
- Amongst the dehydration steps, the value of E_a is on the higher side in cases of group 2 metals and on the lower side in cases of transition metals. The value is maximum in case of magnesium and among the lowest in cases of chromium and iron. The same trend is apparent in cases of dehydration-cum-decomposition steps and it is minimum in cases of cobalt and copper.

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