Thermoanalytical studies on the non-isothermal dehydration and decomposition of \( dl \)-lactates of a series of transition metals

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The non-isothermal decomposition of a series of \( dl \)-lactate hydrates of chromium(III), manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) has been studied with dry air as the purge gas and heating rate programmed at 10 Kmin\(^{-1}\). The \( \alpha-T \) plots obtained from the TG data of none of the purely dehydration steps and the decomposition steps of cobalt(II) and zinc(II) compounds show any induction period, indicating no physical desorption, nucleation or branching while the \( \alpha-T \) plots of the other decomposition phenomena show a period of induction indicating that physical desorption and nucleation are taking place. The TG data of the dehydration steps have also been analyzed using various differential, difference-differential, and integral methods, viz., Freeman-Carroll, Horowitz-Metzger, Coats-Redfern, Zsako, Fuoss-Salyer-Wilson and Karkhanavala-Dharwadkar methods. Values of activation entropy, Arrhenius factor, and order of reaction have been approximated and compared. The values of activation energy \( E \) for the dehydration steps are less than 60 kJmol\(^{-1}\) as expected for removal of weakly bound water of crystallization from such compounds. The entropy of activation \( (\Delta S^\circ) \) values have high magnitude in each case \((<150 JK^{-1}mol^{-1})\) indicating an appreciable degree of rearrangement.

Thermal decomposition of varieties of hydrated and anhydrous metal salts of carboxylic acids (e.g. formic acids\(^{1-3} \)) involving different metals\(^{4-7} \) and sometimes involving a series of carboxylic acids\(^{8} \) have recently been studied using thermogravimetric analysis and the data thus obtained under different specified conditions have been subjected to kinetic and mechanistic analyses. Some carboxylates have also been used frequently to test the efficacy of a new method\(^{9,10} \). But, no systematic attempt has so far been made to study the thermal decomposition of any series of metal lactates. 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 aroused interest in taking up a systematic study of thermal decomposition of \( dl \)-lactates of metals of first transition series.

Out of the various thermoanalytical techniques in vogue, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been recognized as the most convenient ones during the last few decades for the studies of thermal dehydration and decomposition processes. Out of these two, the latter seems to have been overshadowed in recent years by differential scanning calorimetry (DSC) on account of it being a more reliable, precise but versatile and convenient technique for such studies. Thermogravimetry however, still remains the most popular method for studying the kinetics of decomposition of solids and those of gas-solid reactions.

Large number of mathematical models have been proposed and used for studying kinetics and mechanism of such reactions using the data of thermal analyses carried out under both the broad experimental methods viz. isothermal (when the solid reactant is kept under isothermal conditions) and non-isothermal (when the solid is submitted to a gradual increase in temperature-usually linear with time). Of the two methods, which one is superior for obtaining more precise values of kinetic parameters such as activation energy \( E \) and the pre-exponential factor \( A \), has been a subject of considerable debate\(^{10-13} \). While the non-isothermal methods have been criticized on the ground that the kinetic parameters obtained are dependent on local factors or the procedural factors like sample and particle size, compactness, heating rate, gas phase composition, solid porosity etc., protagonists of isothermal methods argue that this situation arises in isothermal methods as well. Such problems are attributed to the complexities of reaction mechanism and lack of proper mechanistic equations considered for the process considered and to the heat and mass transfer effects. In order to get rid of this problem, some\(^{10-16} \) are also in favour of model-free
procedures for obtaining kinetic parameters as in the isoconversional methods. Orfao and Martins have concluded that the model fitting methods are not that much sensitive to experimental errors as the isoconversional methods. Recently, multi-heating rate data have also been recommended for non-isothermal studies. Moreover, it is a well-established fact that minimizing the local factors brings perfection. For example, small sample size minimizes heat and mass transfer phenomena and a purge gas may minimize a build up and rise in the partial pressure of the evolved gas on the reacting/decomposing solid and subsequently the impacts of what is known as the famous Smith-Topley effect in cases of dehydration reactions.

Kinetic analysis of TG data of any dehydration/decomposition method is usually based on the two primary equations (1) and (2).

\[
d\alpha/dt = k f(\alpha) \quad \cdots (1)
\]
\[
k = A \exp(-E/RT) \text{ or } \ln k = \ln A - E/RT \quad \cdots (2)
\]

where \(\alpha\) stands for the fraction of reaction that has taken place at time \(t\) (defined as \(\alpha = (W_0 - W)/(W_0 - W_\infty)\) where \(W\) is the weight of solid and subscripts 0 and \(\infty\) refer to the initial and residual amounts respectively), \(d\alpha/dt\) is the rate of reaction and \(f(\alpha)\) is the mathematical expression in term of \(\alpha\), describing the kinetic and mechanistic step. Many equations relating the rate of solid-state reactions to \(\alpha\) and the mathematical models for the reaction mechanisms (Table I) have been applied to various systems. But sometimes, the decompositions following a particular mechanism have been found to be shifting to another mechanism after some time in isothermal methods.

As enunciated above, the change in partial pressure of the gaseous build up also affects the mechanism that is followed by the decomposition process. Equation (1) can be written in integral form as (3) or can be combined with Eq. (2) to give Eqs (4) and (5):

\[
g(\alpha) = \int d\alpha/f(\alpha) = \int kdt = kt \quad \cdots (3)
\]
\[
\ln [(d\alpha/dt)/f(\alpha)] = \ln A - E/RT \quad \cdots (4)
\]
\[
d\alpha/dt = A \exp(-E/RT)f(\alpha) \quad \cdots (5)
\]

Equations (4) and (5) are a couple of differential forms and Eq. (3) is an integral form which can be rearranged to Eq. (6) within integration limits of \(T_0\) and \(T\) corresponding to the conversions 0 to \(\alpha\) if the reaction is carried out under a linear temperature programme (\(T = T_0 + bT\), where \(b\) stands for the heating rate and \(T_0\) is the initial temperature for the transformation under consideration):

\[
g(\alpha) = \int [d\alpha/f(\alpha)] = A/b \int \exp(-E/RT)dT \quad \cdots (6)
\]

Some important forms of \(g(\alpha)\) have been mentioned (Table 1). However, many authors support the use of empirical kinetic laws of the type \(f(\alpha) = (1-\alpha)^n\) where \(n\) is the order of reaction. On the basis of these fundamental equations and their derivatives, many difference-differential, differential and integral methods have been developed out of

<table>
<thead>
<tr>
<th>Type of mechanism</th>
<th>(f(\alpha))</th>
<th>(g(\alpha))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Zero order</td>
<td>1</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>2) One half order</td>
<td>((1 - \alpha)^{1/2})</td>
<td>(2[1-(1-\alpha)^{1/2}])</td>
</tr>
<tr>
<td>3) Two thirds order</td>
<td>((1 - \alpha)^{2/3})</td>
<td>(3[1-(1-\alpha)^{2/3}])</td>
</tr>
<tr>
<td>4) First order</td>
<td>((1 - \alpha))</td>
<td>(-\ln(1-\alpha))</td>
</tr>
<tr>
<td>5) Three halves kinetics</td>
<td>((1 - \alpha)^{3/2})</td>
<td>(2[(1-\alpha)^{3/2} - 1])</td>
</tr>
<tr>
<td>6) Second order</td>
<td>((1 - \alpha)^2)</td>
<td>((1-\alpha)(1 - \alpha)^2)</td>
</tr>
<tr>
<td>7) Avrami-Erofeev eqn.(n=1.5)</td>
<td>(3/2(1-\alpha)[\ln(1-\alpha)]^{1/3})</td>
<td>([-\ln(1-\alpha)]^{1/3})</td>
</tr>
<tr>
<td>8) Avrami-Erofeev Eqn.(n=2)</td>
<td>((1-\alpha)[\ln(1-\alpha)]^{1/2})</td>
<td>([-\ln(1-\alpha)]^{1/2})</td>
</tr>
<tr>
<td>9) Avrami-Erofeev Eqn.(n=3)</td>
<td>((1-\alpha)[\ln(1-\alpha)]^{2/3})</td>
<td>([-\ln(1-\alpha)]^{2/3})</td>
</tr>
<tr>
<td>10) Avrami-Erofeev Eqn.(n=4)</td>
<td>((1-\alpha)[\ln(1-\alpha)]^{3/4})</td>
<td>([-\ln(1-\alpha)]^{3/4})</td>
</tr>
<tr>
<td>11) 1D diffusion</td>
<td>(1/2\alpha)</td>
<td>(\alpha/2)</td>
</tr>
<tr>
<td>12) 2D diffusion</td>
<td>(-[\ln(1-\alpha)])</td>
<td>(\alpha(1-\alpha)[\ln(1-\alpha)])</td>
</tr>
<tr>
<td>13) 3D diffusion</td>
<td>(3(1-\alpha)^{3/2}/2[1-(1-\alpha)^{1/3}])</td>
<td>([-((1-\alpha)^{3/2})])</td>
</tr>
<tr>
<td>14) Contracting cylinder</td>
<td>(2(1-\alpha)^{1/2})</td>
<td>([1-(1-\alpha)^{1/2}])</td>
</tr>
<tr>
<td>15) Contracting sphere</td>
<td>(3(1-\alpha)^{2/3})</td>
<td>([1-(1-\alpha)^{2/3}])</td>
</tr>
</tbody>
</table>
which six most popular ones\(^{9,30-34}\) (Eqs 7-13) have been used in the present work for the approximation of kinetic parameters of dehydration/first step decomposition of the dl-lactate hydrates of chromium(III), manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) and the results have been compared taking into account the data earlier obtained\(^{5}\) for the zinc compound. Attempts have also been made to find any pattern in the onset temperature of thermal dehydration and thermal decomposition in the series on the pattern of that reported by Valor et al\(^{8}\).

**Materials and Methods**

The dl-lactate hydrates of chromium (III), manganese (II), iron (II), cobalt (II), nickel (II), copper (II) and zinc (II) were synthesized by the usual method\(^{35}\) 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 complexes 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 thermograms of all the dl-lactate hydrates were recorded using dry air as the purge gas with heating rate programmed at 10 Kmin\(^{-1}\). The residues were again analysed for the percentage of metals by dissolving them as usual.

**Results and Discussion**

Like most organic salts\(^{36}\), the dl-lactates of chromium(III), iron(II), nickel(II) and zinc(II)\(^{5}\) 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 weight loss suggest that dehydrations proceeded without any intermediates. The dl-lactates of 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 \(\alpha-T\) plots obtained from the TG data of none of the purely dehydration steps and the decomposition steps of the cobalt (II) and zinc (II) compounds show any induction period indicating no physical desorption, nucleation or branching while the \(\alpha-T\) plots of the other decomposition phenomena show a period of induction thus indicating that physical desorption and nucleation are taking place\(^{37}\). They were tested for the possible mechanistic models using the equations mentioned (Table 1). The initial indications were supported to a great extent and they

<table>
<thead>
<tr>
<th>S.No</th>
<th>Compound</th>
<th>Temperature range</th>
<th>Suggested mode of decomposition</th>
<th>Model followed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CrL(_2)3H(_2)O</td>
<td>(i) 313-553K (ii) 583-773K</td>
<td>CrL(_2)3H(_2)O (\rightarrow) CrL(_2) CrL(_2) (\rightarrow) 1/2Cr(_2)O(_3)</td>
<td>2(^{\text{nd}}) order kinetic (n=2) 3D diffusion</td>
</tr>
<tr>
<td>2</td>
<td>MnL(_2)3H(_2)O</td>
<td>303-553K</td>
<td>MnL(_2)3H(_2)O (\rightarrow) MnO</td>
<td>Avrami-Erofeev (n=1.5)</td>
</tr>
<tr>
<td>3</td>
<td>FeL(_2)5H(_2)O</td>
<td>(i) 318-573K (ii) 583-773K</td>
<td>FeL(_2)5H(_2)O (\rightarrow) FeL(_2) FeL(_2) (\rightarrow) 1/2Fe(_2)O(_3)</td>
<td>2(^{\text{nd}}) order kinetic Avrami-Erofeev (n=1)</td>
</tr>
<tr>
<td>4</td>
<td>CoL(_2)3H(_2)O</td>
<td>303-513K</td>
<td>CoL(_2)3H(_2)O (\rightarrow) CoO</td>
<td>Three half kinetic</td>
</tr>
<tr>
<td>5</td>
<td>NiL(_2)3H(_2)O</td>
<td>(i) 303-455K (ii) 483-643K</td>
<td>NiL(_2)3H(_2)O (\rightarrow) NiL(_2) NiL(_2) (\rightarrow) NiO</td>
<td>2(^{\text{nd}}) order kinetic Avrami-Erofeev (n=3)</td>
</tr>
<tr>
<td>6</td>
<td>CuL(_2)2H(_2)O</td>
<td>303-473K</td>
<td>CuL(_2)2H(_2)O (\rightarrow) CuO</td>
<td>Avrami-Erofeev (n=5)</td>
</tr>
<tr>
<td>7</td>
<td>ZnL(_2)3H(_2)O</td>
<td>(i) 353-463K (ii) 473-813K</td>
<td>ZnL(_2)3H(_2)O (\rightarrow) ZnL(_2) ZnL(_2) (\rightarrow) ZnO</td>
<td>2/3 order kinetic path 1(^{\text{st}}) order kinetic model</td>
</tr>
</tbody>
</table>

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\(^{9}\)Calculation with \(\alpha-T\) plots and equations.

\(^{30}\)Calculation with equation (7).

\(^{31}\)Calculation with equation (8).

\(^{32}\)Calculation with equation (9).

\(^{33}\)Calculation with equation (10).

\(^{34}\)Calculation with equation (11).

\(^{35}\)Calculation with equation (12).

\(^{36}\)Calculation with equation (13).

\(^{37}\)Calculation with equation (14).

---

\(^{5}\)Calculation with equation (15).

\(^{8}\)Calculation with equation (16).

\(^{10}\)Calculation with equation (17).

\(^{11}\)Calculation with equation (18).

\(^{12}\)Calculation with equation (19).

\(^{13}\)Calculation with equation (20).

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\(^{15}\)Calculation with equation (21).

\(^{16}\)Calculation with equation (22).

\(^{18}\)Calculation with equation (23).

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\(^{20}\)Calculation with equation (24).

\(^{21}\)Calculation with equation (25).

\(^{22}\)Calculation with equation (26).

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\(^{24}\)Calculation with equation (27).

\(^{25}\)Calculation with equation (28).

\(^{26}\)Calculation with equation (29).

---

\(^{28}\)Calculation with equation (30).

\(^{29}\)Calculation with equation (31).

\(^{30}\)Calculation with equation (32).

---

\(^{32}\)Calculation with equation (33).

\(^{33}\)Calculation with equation (34).

\(^{34}\)Calculation with equation (35).
were found to be following either an nth order kinetic path or an Avrami-Erofeev equation (Table 2).

The kinetics of the dehydration processes were analysed by means of the following popular methods (Eqs 7-13):

Freeman-Carroll:

\[
(E/2.303R)\Delta T^{-1}/\Delta \log w_r = -n + \Delta \log (dw/dt)/\Delta \log w_r
\]

Horowitz-Metzger:

\[
\ln \left( \frac{w_i}{w_r} \right) = E\Phi/RT_s^2
\]

Coats-Redfern:

\[
\log \left[ \log \left( \frac{(1-\alpha)}{T^2} \right) \right] = \left\{ \log (AR/bE) \right\} \left[ 1 - 2RT/E \right] - E/2.303RT
\]

and for \( n \neq 1 \):

\[
\log \left[ 1 - \left\{ \frac{(1-\alpha)}{T^2} \right\} \left( \frac{1}{1-n} \right) \right] = \left\{ \log (AR/bE) \right\} \left[ 1 - 2RT/E \right] - E/2.303RT
\]

Fuoss-Salyer-Wilson/Karkhanavala-Dharwadkar:

\[
E = \left[ RT_s^2/W_r \right] (dW/dT)\]

Zsako:

\[
\log(AE/Rb) = \log(g(\alpha)) - \log(p(x)) = B
\]

\[
\log A = B + \log Rb - \log E
\]

where \( n \) is the order of reaction, \( w_r \) stands for the difference \( (w_i - w) \), \( w_i \) is the weight loss at completion of reaction \( (W_0 - W_w) \), \( w \) is that up to time \( t \), \( T \) the absolute temperature, \( T_s \) the reference temperature such that at \( T_s \), \( W/W_0 = 1/e \), \( \theta \) the difference \( (T - T_s) \), \( dW/dt \) 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. (12). The values of \( \log(p(x)) \) were taken from the Zsako 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 furnished the value of order of the reaction and the \( E \)-value was obtained from the slope \( (E/2.303R) \). In the Horowitz-Metzger method, the slope was \( (E/RT_s^2) \) and in the Coats-Redfern method, trying equations of different orders searched the most linear plot and the most linear plot furnished activation energy from its slope \( (E/2.303R) \). In the Fuoss-Salyer-Wilson method, the activation energy value was obtained from the point of inflexion in the TG trace. The K-D method involved a plot of \( \alpha \) vs. \( (T_o + \phi) \) where \( \phi = \left( (T_s - T_o)/ (T_s - T_0) \right) \times 100 \) which furnished the point of inflexion leading to the \( E \)-value from Eq. (11). In Zsako 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 Zsako chart, were extrapolated to arrive at a minimum to furnish more appropriate value of the standard deviation in each case and hence that of activation energy.

Table 3—Kinetic parameters of thermal dehydration of dl-lactates of chromium (III), iron (II), nickel (II) and zinc (II)

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CrL₂₃H₂O</td>
<td>Dehyd</td>
<td>( E )</td>
<td>48.50</td>
<td>29.76</td>
<td>26.29</td>
<td>17.02</td>
<td>22.62</td>
<td>17.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( A )</td>
<td>1.666 \times 10⁵</td>
<td>4.723 \times 10⁷</td>
<td>3.46 \times 10⁴</td>
<td>4.35 \times 10⁵</td>
<td>2.76 \times 10⁴</td>
<td>9.99 \times 10⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta S^\circ )</td>
<td>-147.70</td>
<td>-185.87</td>
<td>-160.73</td>
<td>-256.70</td>
<td>-220.07</td>
<td>-247.69</td>
</tr>
<tr>
<td>FeL₂₅H₂O</td>
<td>Dehyd</td>
<td>( E )</td>
<td>29.40</td>
<td>34.83</td>
<td>25.93</td>
<td>27.11</td>
<td>29.10</td>
<td>23.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( A )</td>
<td>1.125 \times 10⁴</td>
<td>3.312 \times 10⁴</td>
<td>6.25 \times 10³</td>
<td>7.02 \times 10⁴</td>
<td>1.34 \times 10³</td>
<td>1.12 \times 10³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta S^\circ )</td>
<td>-188.61</td>
<td>-171.92</td>
<td>-174.36</td>
<td>-211.68</td>
<td>-206.29</td>
<td>-226.94</td>
</tr>
<tr>
<td>NiL₂₃H₂O</td>
<td>Dehyd</td>
<td>( E )</td>
<td>34.86</td>
<td>32.70</td>
<td>35.89</td>
<td>35.71</td>
<td>34.44</td>
<td>33.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( A )</td>
<td>1.382 \times 10³</td>
<td>9.8 \times 10⁶</td>
<td>8.55 \times 10⁴</td>
<td>1.108 \times 10³</td>
<td>3.95 \times 10⁴</td>
<td>4.41 \times 10⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta S^\circ )</td>
<td>-140.722</td>
<td>-246.73</td>
<td>-190.45</td>
<td>-188.30</td>
<td>-196.87</td>
<td>-199.20</td>
</tr>
<tr>
<td>ZnL₂₃H₂O</td>
<td>Dehyd</td>
<td>( E )</td>
<td>49.86</td>
<td>70.44</td>
<td>67.39</td>
<td>46.27</td>
<td>45.59</td>
<td>52.64</td>
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<tr>
<td></td>
<td></td>
<td>( A )</td>
<td>2.02 \times 10⁵</td>
<td>2.51 \times 10²</td>
<td>5.13 \times 10⁶</td>
<td>5.67 \times 10³</td>
<td>3.37 \times 10⁵</td>
<td>1.50 \times 10⁵</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta S^\circ )</td>
<td>-135.42</td>
<td>-201.51</td>
<td>-118.97</td>
<td>-175.58</td>
<td>-179.71</td>
<td>-167.49</td>
</tr>
</tbody>
</table>

\( E \) is in kJmol⁻¹, \( A \) in s⁻¹, \( \Delta S^\circ \) in JKmol⁻¹
Table 4—Kinetic parameters of decomposition of the lactate hydrates of manganese (II), cobalt (II) & copper (II) and those of the zinc lactate

<table>
<thead>
<tr>
<th>Composition</th>
<th>Step</th>
<th>Kinetic parameters</th>
<th>F-C</th>
<th>H-M</th>
<th>C-R</th>
<th>F-S-W</th>
<th>K-D</th>
<th>Zsako</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnL₂·3H₂O</td>
<td>Dehydr-cum-decomp.</td>
<td>E</td>
<td>27.28</td>
<td>65.14</td>
<td>24.13</td>
<td>23.36</td>
<td>24.08</td>
<td>24.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>1.193×10⁴</td>
<td>1.241×10⁴</td>
<td>4.312×10⁴</td>
<td>1.439×10⁴</td>
<td>2.10×10⁴</td>
<td>1.111×10⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n</td>
<td>2.85</td>
<td>1/3</td>
<td>2</td>
<td>—</td>
<td>—</td>
<td>2</td>
</tr>
<tr>
<td>CoL₂·3H₂O</td>
<td>Dehydr-cum-decomp.</td>
<td>E</td>
<td>45.95</td>
<td>20.60</td>
<td>11.16</td>
<td>17.84</td>
<td>18.04</td>
<td>14.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>5.68×10⁴</td>
<td>1.10×10⁴</td>
<td>9.325×10⁴</td>
<td>5.30×10⁴</td>
<td>1.34×10⁴</td>
<td>2.60×10⁴</td>
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<td>n</td>
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<tr>
<td>CuL₂·2H₂O</td>
<td>Dehydr-cum-decomp.</td>
<td>E</td>
<td>23.93</td>
<td>19.46</td>
<td>16.16</td>
<td>29.56</td>
<td>24.13</td>
<td>23.36</td>
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<td>A</td>
<td>3.792×10⁴</td>
<td>1.32×10⁴</td>
<td>2.955×10⁴</td>
<td>4.35×10⁴</td>
<td>7.01×10⁴</td>
<td>1.711×10⁴</td>
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<td>ΔSᵣ</td>
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<td>-266.14</td>
<td>-125.29</td>
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<td>-232.99</td>
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<tr>
<td>ZnL₂·3H₂O</td>
<td>Decomp. only</td>
<td>E</td>
<td>104.24</td>
<td>81.73</td>
<td>65.63</td>
<td>55.71</td>
<td>58.79</td>
<td>66.10</td>
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<td>A</td>
<td>1×10¹⁰</td>
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<td>5.575×10³</td>
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<td>ΔSᵣ</td>
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</table>

E is in kJmol⁻¹, A in s⁻¹, ΔSᵣ in JKmol⁻¹

The values of A were also obtained using the methods described above. The values of entropy of activation were obtained using the thermodynamic relation (14):

$$ΔS^\# = 2.303R \log(Ah/kT_{1/2})$$  ... (14)

where $h$ is the Planck's constant, $k$ the Boltzmann constant and $T_{1/2}$ the temperature at which half of the transformation is complete. The values of the kinetic parameters have been put in Table 3.

The onset temperatures of dehydrations do not follow any pattern on the line of calcium salts of the aliphatic series of carboxylates recently reported by Valor et al.⁴. The values of activation entropy (<−150 JK⁻¹mol⁻¹ in each case) indicate appreciable rearrangements among various degrees of freedom in the formation of the activated complex. The values of activation energy are within the range (<60 kJmol⁻¹) as expected for removal of weakly bound water of crystallization from such compounds.⁴⁸,⁴⁹ The low values of $E$ for the overall single step decomposition processes of the manganese, cobalt and copper compounds are apparently behind the overlapping of the processes unlike that in case of the decomposition step of the zinc compound for example (Table 4).

References
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