4.1 Introduction

The thermal analysis of a material is associated with the rate at which materials undergo physical and chemical transitions. The associated energy and mass changes with temperature on heating at a constant rate are studied. In thermogravimetric analysis, the mass of the sample is recorded continuously as a function of temperature on heating in an inert environment, at a controlled rate [1-3]. Thermogravimetric analysis (TGA) curves are characteristic for a given compound or system due to the unique sequence of physiochemical reactions that occur at definite temperatures and at rates governed by the molecular structure. Changes in the mass of the sample occur as a result of the rupture and formation of various chemical bonds at elevated temperatures leading to the evolution of volatile products or formation of reaction products. Hence the TGA curve gives information regarding the thermodynamics and kinetics of various chemical reactions, reaction mechanisms and final reaction products.

In differential thermal analysis (DTA), the difference in temperature of the sample and a thermally inert reference material are measured as a function of temperature. When the sample is heated, it absorbs or liberates
energy depending on the transitions taking place. The corresponding deviation of the sample temperature from that of the reference ($\Delta T$) versus the programmed temperature ($T$) is recorded and it explains whether the transition is endothermic or exothermic. The DTA studies in conjunction with TGA provide detailed information regarding the dehydration, decomposition and phase transitions of a material during heating. The thermal data helps to assess the stability of the material under thermodynamic conditions and to fix the reaction kinetics (4-10). A proper understanding of the decomposition properties will throw light on the stability of the crystal.

4.2 Experimental

The thermal characteristics of all the five grown urinary crystals were studied using Shimadzu thermo balance. The instrument consists of a sensitive analytical balance, a furnace and a microprocessor for data acquisition and display. The temperature range selected for the present study was from 35-1000°C in argon atmosphere. The decomposition stages and corresponding activation energies are determined using Coats-Redfern relation [11]. This method was chosen in particular because it allows the determination of both activation energy and the order of reaction simultaneously.

4.3 Theory

In the decomposition reaction let of ‘a’ grams of compound L (solid) be converted into ‘b’ grams of solid product (M) and ‘c’ grams of gas (N).

$$a \ L(s) \rightarrow b \ M(s_i) + c \ N(g)$$
The fraction $\alpha$, of $L(S)$ decomposed at time $t$ is given by

$$\frac{d\alpha}{dt} = K(1-\alpha)^n$$  \hspace{1cm} (4.1)

$n$ is the order of the reaction and $K$ is the reaction rate constant. The reaction rate constant and activation energy $E$ are related through

$$K = A \exp(-E/RT)$$  \hspace{1cm} (4.2)

where $A$ is the frequency factor and $T$ is the temperature expressed in Kelvin scale.

When the heating rate is linear,

$$\beta = \frac{dT}{dt}$$  \hspace{1cm} (4.3)

Combining equations (4.1), (4.2) and (4.3), rearranging and integrating

$$\int_{0}^{\beta} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{0}^{T} \frac{e^{-\frac{E}{RT}}}{dT}$$  \hspace{1cm} (4.4)

The integral on the right hand side is evaluated by making the substitution $u = E/RT$ and using the relation

$$\int e^{-u} \cdot du \approx u^{-b} \cdot e^{-u} \cdot \sum_{n=0}^{\infty} (-1)^{n} \frac{(b)^{n}}{u^{n+1}}$$

The equation (4.4) becomes

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^{2}}{\beta E} \left[ 1 - \frac{2RT}{E} \right] e^{-E/RT}$$  \hspace{1cm} (4.5)

Let $\gamma = (1-\alpha)$ and $p = (1-n)$, taking log of both sides

$$\log \left( \frac{1-(\gamma)}{\gamma^{p}} \right) = \log \frac{AR}{\beta E} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad \text{for} \quad n \neq 1 \quad \text{--------- (4.6)}$$

$$\log \left( -\log \frac{\gamma}{T^{2}} \right) = \log \frac{AR}{\beta E} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad \text{for} \quad n = 1, \quad \text{--------- (4.7)}$$
Hence a plot of \( \log \left( \frac{1 - \gamma^2}{T^2} \right) \) against \( \frac{1}{T} \), for \( n \neq 1 \) and a plot of

\[
\log \left( -\log \frac{\gamma}{T} \right) \text{ against } \frac{1}{T}, \text{ for } n = 1 \text{ results in a straight line. The activation energy } E \text{ is determined from the slope } \left( -\frac{E}{2.3R} \right) \text{ for the best linear fit value of 'n' the order of the reaction.}

W.E. Garner [12] theoretically justifies the order of reaction as 0, 1/2, 2/3, 1 and 3/2 in solid-state kinetics. The best linear fit gives the appropriate order of the reaction.

4.4 Results and Discussions

(a) Decomposition of calcium oxalate monohydrate (whewellites)

In the decomposition of whewellites (figure 4.1) the following three-stage sequence is proposed. The inter molecularly bonded water molecule co-ordinated with calcium oxalate in the crystal gets released at 200°C. Calcium oxalate gets decomposed to calcium carbonate with the liberation of calcium monoxide at 500°C. In the third stage of the decomposition, calcium carbonate decomposes to calcium oxide and carbon dioxide (13, 14). Corresponding to the three stages of decomposition, the DTA curve shows three endothermic peaks at 220°C, 480°C and 800°C. The activation energy and order of reaction are evaluated and are tabulated in table 4.1.

\[
\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \xrightarrow{116-200^\circ\text{C}} \text{CaC}_2\text{O}_4 - \text{H}_2\text{O}
\]

\[
\text{CaC}_2\text{O}_4 \xrightarrow{200-500^\circ\text{C}} \text{CaCO}_3 - \text{CO}
\]

\[
\text{CaCO}_3 \xrightarrow{500-790^\circ\text{C}} \text{CaO} - \text{CO}_2
\]
**Table 4.1:** Activation energy and order of reaction for the decomposition of whewellite

<table>
<thead>
<tr>
<th>Decomposition stages and temperature range</th>
<th>Nature of reaction</th>
<th>Heating Rate Deg/min</th>
<th>Activation Energy KJ/mole</th>
<th>Order of Reaction 'n'</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 116-200°C</td>
<td>Endo dehydration</td>
<td>5</td>
<td>140.99</td>
<td>2/3</td>
<td>12.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.94</td>
</tr>
<tr>
<td>II 200-500°C</td>
<td>Endo dehydration</td>
<td>5</td>
<td>92.234</td>
<td>2/3</td>
<td>18.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.28</td>
</tr>
<tr>
<td>III 500-790°C</td>
<td>Endo decarboxilation</td>
<td>5</td>
<td>92.234</td>
<td>2/3</td>
<td>18.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.28</td>
</tr>
</tbody>
</table>

**Figure 4.1:** TG(---/DTA(---) of whewellite

(b) **Decomposition of dicalcium phosphate dihydrate (brushites)**

In the decomposition of dicalcium phosphate dihydrate (brushites) the following sequence is proposed. As indicated in the TG, brushites starts decomposing at about 116°C and the process is completed at 425°C when it is reduced to the pyrophosphate form. The process of decomposition involves two different stages. The first stage is a dehydration
step and continues up to 190°C and results in the elimination of a water molecule. In the second stage (from 190°C to 425°C) two molecules of CaHPO₄·H₂O combine and results in the elimination of three water molecules leading to the formation of calcium pyrophosphate, which is stable for a long range of temperature. The corresponding DTA spectrum shows endothermic peaks at 150°C and 200°C. The corresponding activation energy and order of reaction are tabled in table 4.2.

\[
\text{CaHPO}_4 \cdot 2\text{H}_2\text{O } \xrightarrow{116^\circ - 190^\circ \text{C}} \text{CaHPO}_4 \cdot \text{H}_2\text{O} - \text{H}_2\text{O}
\]

\[
2\text{CaHPO}_4 \cdot \text{H}_2\text{O } \xrightarrow{190^\circ - 425^\circ \text{C}} \text{Ca}_2\text{P}_2\text{O}_7 - 3\text{H}_2\text{O}
\]

Figure 4.2: TG(--)/DTA(---) of Brushites
Table 4.2: Activation energy and order of reaction for the decomposition of brushites

<table>
<thead>
<tr>
<th>Decomposition stages and temperature range</th>
<th>Nature of reaction</th>
<th>Heating Rate Deg/min</th>
<th>Activation Energy KJ/mole</th>
<th>Order of Reaction</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 600-190°C</td>
<td>Endo dehydration</td>
<td>5</td>
<td>91.2326</td>
<td>1</td>
<td>16.6</td>
</tr>
<tr>
<td>II 190°C-425°C</td>
<td>Endo dehydration</td>
<td>5</td>
<td>85.6325</td>
<td>0</td>
<td>15.7</td>
</tr>
</tbody>
</table>

(c) Decomposition of Ammonium magnesium phosphate hexahydrate (Struvites)

In the decomposition of ammonium magnesium phosphate hexahydrate crystals, the following sequence is proposed. As indicated in the TG (figure 4.3), struvites start decomposing at about 60°C and the process is completed at 425°C when it is reduced to the pyrophosphate form. The process of decomposition involves two different stages. The first stage is an endo dehydration and an endo deammonation which continues up to 190°C resulting in the elimination of three water molecules and an ammonia molecule. In the second stage (190°C - 425°C) two molecules of MgHPO₄·3H₂O combine and results in the elimination of seven water molecules leading to the formation of magnesium pyrophosphate, which is stable over a long range of temperature. The process is in agreement with the proposed structure. Two endothermic curves at 150°C and 190°C and an exothermic peak at 690°C characterize the DTA curves. The corresponding activation energy and order of reaction are tabulated in table 4.3.
\[
\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow{60-190^\circ C} \text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \\
\text{NH}_3 + 3\text{H}_2\text{O}
\]

\[
2\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \xrightarrow{190-425^\circ C} \text{Mg}_2\text{P}_2\text{O}_7 \\
7\text{H}_2\text{O}
\]

**Figure 4.3:** TG(—)/DTA(--•) of struvites

<table>
<thead>
<tr>
<th>Decomposition stages and temperature range</th>
<th>Nature of reaction</th>
<th>Heating Rate Deg/min</th>
<th>Activation Energy KJ/mole</th>
<th>Order of Reaction (n)</th>
<th>Observed Mass loss %</th>
<th>Calculated Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 60-190°C</td>
<td>Endo dehydration &amp; Endo deammonation</td>
<td>5</td>
<td>140.99</td>
<td>2/3</td>
<td>12.56</td>
<td>13.94</td>
</tr>
<tr>
<td>II 190-425°C</td>
<td>Endo dehydration</td>
<td>5</td>
<td>92.234</td>
<td>2/3</td>
<td>18.03</td>
<td>17.28</td>
</tr>
</tbody>
</table>

**Table 4.3:** Activation energy and order of reaction for the decomposition of struvites
(d) Decomposition of Uric acid

Uric acid undergoes single stage decomposition in the temperature range 220-540°C. Almost 95.82% of the total mass gets decomposed during this stage with only carbon remaining (figure 4.4). In this process methane, carbon monoxide and nitrogen are eliminated and corresponding thermal parameters are tabulated in table 4.4.

\[
C_5H_4N_4O_3 \xrightarrow{220-540^0C} C
\]

\[CH_4 + 3CO + 2N_2\]

**Figure 4.4:** TG of Uric Acid

<table>
<thead>
<tr>
<th>Decomposition stages and temperature range</th>
<th>Nature of reaction</th>
<th>Heating Rate Deg/min</th>
<th>Activation Energy KJ/mole</th>
<th>Order of Reaction ( n )</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 220-540°C</td>
<td>Endothermic</td>
<td>5</td>
<td>68.92</td>
<td>3/2</td>
<td>95.82</td>
</tr>
</tbody>
</table>

**Table 4.4:** Activation energy and order of reaction for the decomposition of uric acid
(e) Decomposition of Cystine

Cystine undergoes a two-stage decomposition. The decomposition in the first stage is a fast one in the temperature range 220-340°C with the liberation of carbon dioxide, carbon monoxide, nitrogen, hydrogen sulfide and methane. This is followed by a slow decomposition between 340 and 720°C with carbon as the residue (figure 4.5). The corresponding thermal parameters are tabled in table 4.5.

\[
\text{C}_6\text{H}_2\text{O}_4\text{S}_2\text{N}_2 \xrightarrow{220-340^\circ\text{C}} \text{C}_2\text{H}_4 \\
1.5\text{CO}_2 + \text{CO} + \text{N}_2 + 2\text{H}_2\text{S} + \text{CH}_4
\]

\[
\text{C}_2\text{H}_4 \xrightarrow{340-720^\circ\text{C}} 0.5\text{C} \\
1.5\text{C} + 2\text{H}_2
\]

Figure 4.5: TG of Cystine
Decomposition stages and temperature range | Nature of reaction | Heating Rate Deg/min | Activation Energy KJ/mole | Order of Reaction | Mass loss %
---|---|---|---|---|---
I  220-340°C | Endothermic | 5 | 32.4 | 1 | 85.82 85.83
II  340-720°C | Endothermic | 5 | 57.56 | 1/2 | 11.84 11.6

**Table 4.5:** Activation energy and order of reaction for the decomposition of cystine

The thermal analysis of all the five urinary crystals carried out shows that brushites, struvites and cystine undergo a two-stage decomposition pattern whereas whewellite alone has a three-stage decomposition. Uric acid has mono stage decomposition. The long lasting end products in these samples are i) CaO ii) Ca$_2$P$_2$O$_7$ iii) Mg$_2$P$_2$O$_7$ and iv) C. All of them are solid compounds. Cystine and uric acid being pure organic compounds, carbon is obtained as end product. Calcium oxide is the end product obtained in the decomposition of whewellite. Pyrophosphate derivatives are obtained as the end products for brushite and struvite. There is a perfect match between the observed mass loss and the theoretically calculated mass loss in all cases within the limits of the experimental error confirming the reaction route assumed. The activation energies calculated are the highest for the decomposition of whewellite followed by those for struvites.

**References**


6) Dretler S.P; J. Urol. 1988, **139**, 1124.


9) Vimal S.Joshi and Joshi M.J; Ind.J.Physics. 2001, **75A (2)**, 159.


