

Thermal Phases in Gel-Grown Cadmium Oxalate Single Crystals

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Thermogravimetric (TG) and Differential thermal (DT) analysis carried out for studying thermal kinetics and mechanism of phase changes of gel-grown crystals of cadmium oxalate ($\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$). The material turns out to be trihydrated. The obtained experimental data show that the material is thermally stable up to 64 °C, beyond which it exhibits marked tendency to structural decomposition. The process occurs in three phases until, ultimately, cadmium oxide is obtained. The energies of the reactions involved and the mechanism of phase change at each stage have been examined. The kinetic parameters such as activation energy, order of reaction, frequency factor and entropy are evaluated from non-mechanistic equation for thermal dehydration.

Keywords: Thermogravimetric analysis, Differential thermal (DT) analysis, Phase transition, Activation Energy, Frequency factor

1. Introduction

Thermal methods of investigations, generally referred to as thermoanalytic techniques,¹ have found wide application in material characterization, since these methods essentially depend on measurement of the changes in physicochemical property as a function of increasing temperature with time.^{2,3} An organometallic compound $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ being sparingly soluble in water is crystallized successfully by gel method. The study of thermal analysis⁴ is significant for knowing different phases of stability, analyzing and characterizing wide variety of materials for chemical reactions, decomposition, reaction kinetics and mechanisms etc. Hence the grown crystals of cadmium oxalate have been subjected to thermal treatment in air and nitrogen atmosphere, using gravimetric and differential thermal techniques.

2. Experimental Details



Single crystals with average dimension $3 \times 4 \times 1 \text{ mm}^3$ were grown using the controlled three dimensional diffusion of aqueous CdCl_2 through agar gel impregnated with oxalate ions.⁵

Thermogravimetric (TG) and differential thermal (DT) data were obtained from ambient temperature to 600°C in steps of $10^\circ\text{C}/\text{min}$. with ‘Perkin Elmer-TGA 7’ and ‘Perkin Elmer- DTA 7’ analyzer, respectively. The thermograms have been used for evaluation of some important kinetic parameters in respect of the decomposition phases of cadmium oxalate single crystals.

3. Results and Discussion

3.1 Evaluation of kinetic parameters using TG and DTA Thermogram

The recorded thermogram (Fig. 1a) is first analysed here to obtain information about the percentage weight loss at different temperatures and hence about the thermal stability and kinetics of dissociation of the crystals. Methods for determination of the activation energy from thermogravimetric curve are available in literature.^{6,7,8} A basic method for the interpretation of thermogravimetric traces⁹ is described quantitatively by Eq. 1

$$-\frac{df}{F^n} = \frac{k_0}{a} \exp\left(-\frac{E}{RT}\right) dT \quad (1)$$

Where F denotes the fraction of reactant remaining at the end of pyrolysis, n is the reaction order, k_0 is the pre-exponential part of the rate constant, a is the rate of temperature rise, R is the gas constant and T is the absolute temperature.

When a crystal is heated at a uniform rate of 10°Cmin^{-1} , its weight is found to be lost as a function of the temperature applied. Figure 1a shows the TG thermogram for Cadmium oxalate in air atmosphere. Evidently the phase change begins at the 64°C and the course of dehydration went on upto 360°C . During the temperature range weight loss of 49.6% had occurred and the crystal reduced ultimately to the basic oxide of cadmium as the final stable product. The first stage of transformation is, in fact, the dehydration, which starts at 64°C and continues upto, or terminates at 150°C . The net weight loss (21.4%) as observed between 64 and 150°C corresponds to loss of three water molecules, suggesting that the grown crystal were initially trihydrated and hence the chemical

formula $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. The coordinated three molecules of water lost during this phase change leads to the formation of anhydrous cadmium oxalate as per the reaction (i) given in Table 1. The second phase transition sets in at around 220 °C and is completed at around 310 °C, resulting into the formation of an intermediate product, viz, cadmium carbonate with the loss of carbon monoxide, represented by reaction (ii). This stage of reaction corresponds numerically to 11.08% of the total weight loss. Then, in the third phase of decomposition which seemingly occurs in the temperature interval of 310 °C to 360 °C, the cadmium carbonate is turned into basic oxide of cadmium as the final product, following the reaction (iii), as confirmed by 17.12% of the total mass observed to be lost. The final product CdO remains fairly, reasonably stable.

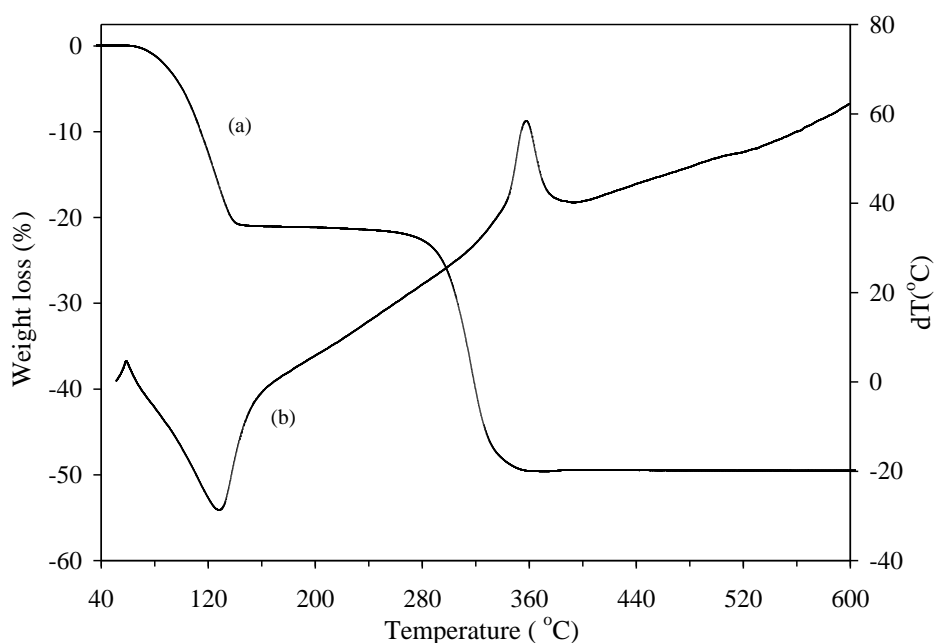


Figure 1. Simultaneous (a) TGA-(b) DTA curve recorded for $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ crystal in air atmosphere.

In the DTA thermogram of Fig. 1b the first well-defined, distinct endothermic peak at 127 °C within the temperature range 60-160°C may be attributed to the removal of the co-ordinated water molecules. The second endothermic peak at 360°C is due to the decomposition of anhydrous cadmium oxalate, accompanying the removal of carbon monoxide and then after the formation of cadmium oxide as the final product compound, accompanied by issuing out of carbon dioxide (third step).

3.1 Thermal Kinetics

The following models are used to evaluate the kinetic parameters of solid-state phase changes with the help of TGA thermogram.

3.1.1 Piloyan - Novikova (PN) relation⁷

Using van Krevelen's⁹ interpretation given in Eq. 1, Piloyan - Novikova simplified by assuming that E is determined at $\alpha \leq 0.5$, to

$$\log\left(\frac{\alpha}{T^2}\right) = \log\left(\frac{ZR}{E\beta}\right) - \frac{E}{2.30RT} \quad (2)$$

where β is the heating rate, Z is the Frequency factor (min^{-1}).

A graphical plot of $\log(\alpha/T^2)$ against $1/T$ (Fig. 2) yields a straight line. From the slope and intercept, activation energy and frequency factor respectively are calculated (Table 2). The main advantage of this method is that reaction order is not needed be determined first.

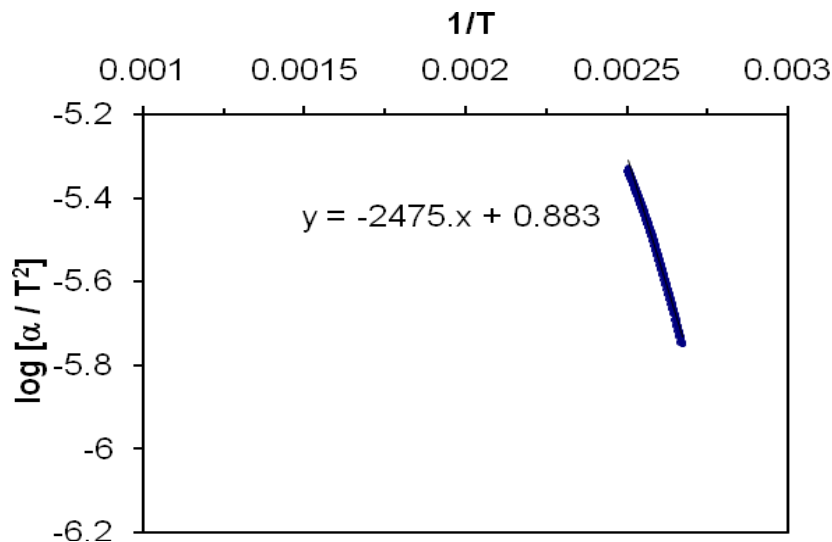


Figure 2. Graphical plot of Piloyan-Novikova (PN) relation.

3.1.2 Coats – Redfern (CR) relation⁸

With the reaction $aA(s) \rightarrow aB(S) + cC(g)$, the rate of disappearance of A may be expressed as

$$\log \left(\frac{g(\alpha)}{T^2} \right) = \log \left(\frac{ZR}{E\beta} \right) - \frac{E}{2.30RT} \quad (3)$$

where $g(\alpha) = [-\log(1-\alpha)]^{1-n}$

The activation energy, E is calculated from the slope of the straight line obtained on plotting L.H.S. of the Eq. (2) against $1/T$ (Fig. 3) and Z from the intercept (Table 2). Hence the values of entropy S are obtained, using the equation

$$Z = \frac{kT_m}{h} \cdot \exp \frac{S}{R}$$

where k is Boltzmann's constant, h is Planck's constant, Z =Pre-exponential factor.

The following model is used to evaluate the thermal kinetics in respect of the grown crystals with the help of DTA thermogram.

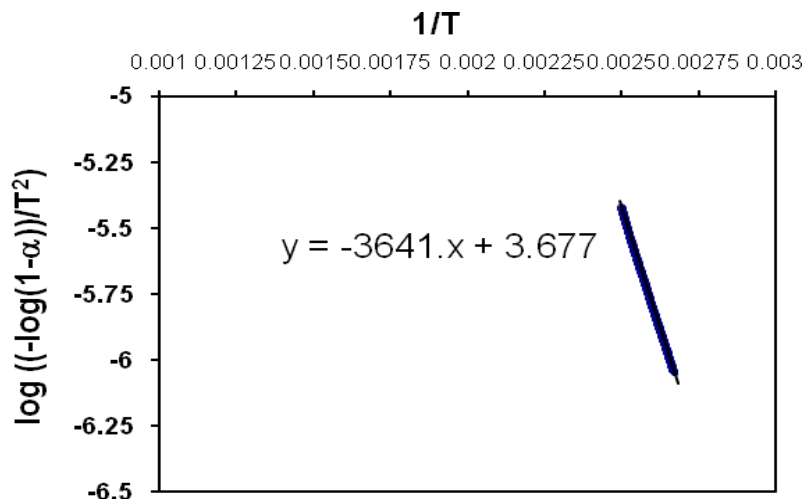


Figure 3. Graphical plot of Coats-Redfern (CR) relation.

3.1.3 Borchardt and Daniels (BD) relation²

For the case of a first order dissociation reaction, we have

$$k = \frac{C_p \left(\frac{d\Delta T}{dt} \right) + K\Delta T}{K(A-a) - C_p\Delta T} \quad (4)$$

The quantities $C_p \frac{d\Delta T}{dt}$ and $C_p\Delta T$ are usually an order of magnitude smaller than the quantities to which they are added and subtracted. Neglecting these smaller terms, Eq. 4

leads to
$$k = \frac{\Delta T}{(A-a)} \quad (5)$$

$$\ln k = \ln Z - \frac{E}{RT} \quad (6)$$

where k is the Specific reaction rate constant (min^{-1}), A is the Total area of peak ($\text{min} \cdot ^\circ\text{C}$), ΔT is the Peak height at any temperature $T(^{\circ}\text{C})$, a is the Area of the peak at temperature $T(\text{min} \cdot ^\circ\text{C})$.

The plot of $\ln k$ against $1/T$ (Fig. 4) is used to calculate the activation energy from the fitted slope and the frequency factor from the intercept (Table 2).

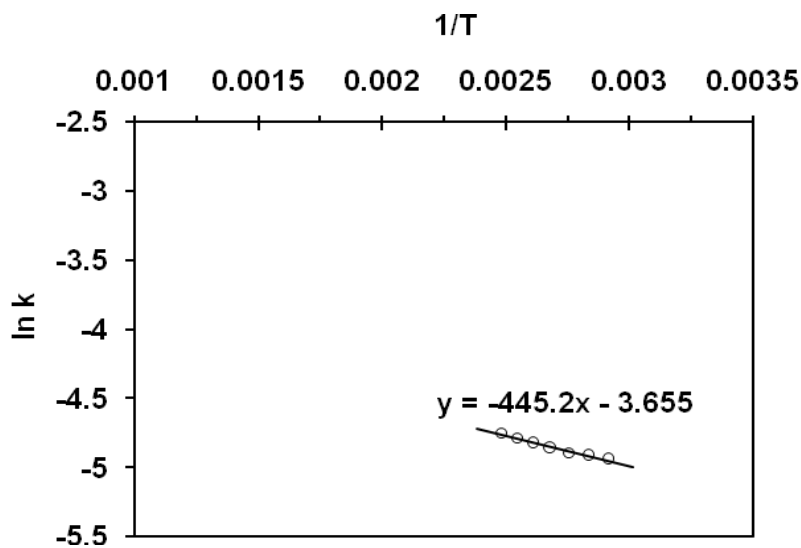


Figure 4. Graphical plot of Borchardt-Daniels (BD) relation.

Table 1. TGA results of phases of Cadmium oxalate in air.

| Step | Temp. Range (°C) | DTA Peak Temp. (°C) | Mass loss % | | Reaction involved |
|------|------------------|---------------------|-------------|--------|---|
| | | | Obs. | Cal. | |
| I | 64-150 | 127.37 | 21.4 | 21.338 | $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{CdC}_2\text{O}_4 + 3\text{H}_2\text{O}(\text{i})$ |
| II | 220-310 | - | 11.08 | 11.007 | $\text{CdC}_2\text{O}_4 \rightarrow \text{CdCO}_3 + \text{CO}(\text{ii})$ |
| III | 310-360 | 357 | 17.12 | 17.294 | $\text{CdCO}_3 \rightarrow \text{CdO} + \text{CO}_2(\text{iii})$ |

Table 2. Kinetic parameters evaluated from non-mechanistic equations for thermal phases $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ for the first step of transformation.

| Step | Temp. Range (°C) | DTA Peak Temp(°C) | Mass loss % | | Reaction involved |
|------|------------------|-------------------|-------------|--------|---|
| | | | Obs. | Cal. | |
| I | 64-150 | 127.37 | 21.4 | 21.338 | $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{CdC}_2\text{O}_4 + 3\text{H}_2\text{O}(\text{i})$ |
| II | 220-310 | - | 11.08 | 11.007 | $\text{CdC}_2\text{O}_4 \rightarrow \text{CdCO}_3 + \text{CO}(\text{ii})$ |
| III | 310-360 | 357 | 17.12 | 17.294 | $\text{CdCO}_3 \rightarrow \text{CdO} + \text{CO}_2(\text{iii})$ |

4. Conclusion

In cadmium oxalate crystal there are three water molecules present which render the crystal unstable at higher temperature. The thermal phase changes in the air atmosphere suggest the material to be unstable even at moderate temperatures. The activation energy (also the frequency factor) of dehydration step is the lowest in all the other stages of decomposition, implying low energy involved for loosening of the bonded water molecules. Activation energy

of the third stage of decomposition is the highest, implying that oxalate to oxide conversion is indeed a harder reaction.

References and Notes

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