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Thermal analysis of calcium oxalate samples obtained by various preparative routes

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Abstract

The thermal analysis of various calcium oxalate samples obtained by precipitation from aqueous solutions, in the presence of urea and from methanol is reported. The occurrence of different hydrate forms is established and a kinetic analysis for the dehydration and subsequent decomposition stage establishes that the Arrhenius parameters are significantly altered by the preparative route, the initial dehydration, and the environmental conditions of the thermal analysis experiment. © 1997 Elsevier Science B.V.

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1. Introduction

Calcium oxalate exists in various hydrated forms. The monohydrate ($CaC_2O_4{\cdot}H_2O$) is the usually described form and as such is commonly used in thermogravimetry (TG) to establish both the accepted temperature regions in which decomposition occurs and also the accuracy of the mass losses taking place in the various stages [1]. For calcium oxalate monohydrate the following sequence is commonly reported

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 \rightarrow CaCO_3 \rightarrow CaO$$

The dehydration is an endothermic event in an atmosphere of dry nitrogen and air followed in the next step by the loss of carbon monoxide to give calcium carbonate, and finally loss of carbon dioxide to form calcium oxide; both these stages are also endothermic events.

In studies on gall stones, calcium oxalate is often described as existing as the dihydrate, [2,3] but on storage there is quite often a significant change in the appearance of the gall stone. It would seem that a low temperature dehydration may be occurring so that dehydration is possible.

$$CaC_2O_4 \cdot 2H_2O \rightarrow CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4$$

In recent studies on calcium oxalate preparations in the presence of methanol, the formation of the trihydrate is reported [4]. There are also reports that isolating calcium oxalate from certain plants produces the dihydrate form [5]. It is speculated that preparations from an ionic environment favor the production of the monohydrate while preparation from a covalent environment favors the production of the dihydrate. In view of these reports it was decided to attempt the

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preparation of the various forms of the calcium oxalate to identify them as far as possible and to study their thermal decomposition by thermal analysis using a simultaneous TG–DTA unit.

2. Materials and methods

The thermal analysis was carried out using a simultaneous TG–DTA unit from TA instruments, model no. 2960. Platinum crucibles were used to hold the samples, with an empty crucible used as the reference. An inert atmosphere was maintained using dry nitrogen at a flowing rate of 100 ml min^{-1}. The commercial calcium oxalate was purchased from Fisher Scientific. Calcium nitrate, oxalic acid and urea were also supplied by Fisher Scientific. Methanol was supplied by J. T. Baker. Calcium oxalate was prepared by using calcium nitrate and urea solutions and mixing these with equimolar solutions of oxalic acid in urea at 0°C, 5°C, room temperature and 70°C. The samples after precipitation were air dried at ambient temperature. Similarly in another set of experiments, the same method was used, but instead of urea, methanol was used. The list of preparations is set out in Table 1.

3. Results and discussions

The theoretical mass loss for various stages in calcium oxalate monohydrate decomposition, via the anhydrous salt, the carbonate and the oxide are presented in Table 2, together with similar data for dihydrate. The TG–DTG plot for typical samples is shown in Figs. 1 and 2 and the mass losses and DTG peak temperatures given in Table 3. Samples prepared in the presence of urea and air dried displayed an increased dehydration stage coming very close to that for the dihydrate (see Table 2), while the sample prepared in the presence of urea at a high temperature (70°C) led to the formation of monohydrate. Increasing the concentration of urea beyond 1.5 M gave data which were difficult to interpret from the thermal analysis alone possibly due to an inability to wash out all the occluded urea from the structure. Samples produced using methanol showed a dehydration stage corresponding to the monohydrate.

X-ray powder diffraction data identified sample CaC_2O_4 (0.75 M) 70°C as the monohydrate similar to the commercial sample (CaC_2O_4 (commercial)) with samples CaC_2O_4 (0.75) 5°C, and CaC_2O_4

Table 2
Summary of the theoretical changes expected in the decomposition of calcium oxalate monohydrate and calcium oxalate dihydrate

Compound formed	% Residue
Calcium oxalate monohydrate $CaC_2O_4{\cdot}H_2O$	
CaC_2O_4	87.7
$CaCO_3$	0.5
CaO	38.4
Calcium oxalate dihydrate $CaC_2O_4{\cdot}2H_2O$	
$CaC_2O_4{\cdot}H_2O$	89.0
CaC_2O_4	78.1
CaO_3	61.0
CaO	34.2

Table 1
Preparation of calcium oxalate hydrates studied in the present project and dried at room temperature as described in the text

Designation	Preparation summary
CaC_2O_4 (commercial)	Commercial sample from Fisher Scientific and described as $CaC_2O_4{\cdot}H_2O$
CaC_2O_4 (0.75 M) 0°C	50 ml solution of calcium nitrate (0.5 M) + 50 ml of urea solution (0.75 M) mixed with 50 ml solution of oxalic acid (0.5 M) + 50 ml of urea (0.75 M) at 0°C
CaC_2O_4 (0.75 M) 5°C	As above but prepared at 5°C
CaC_2O_4 (0.75 M) RT	As above but prepared at room temperature
CaC_2O_4 (0.75 M) 70°C	As above but prepared at 70°C
CaC_2O_4 (1.5 M) 5°C	In this preparation the urea was at 1.5 M and the preparation temperature 5°C
CaC_2O_4 (1.75 M) 5°C	In this preparation the urea was at 1.75 M and the preparation temperature 5°C
CaC_2O_4 in CH_3OH 5°C	In this preparation 50 ml of calcium nitrate (0.5 M) was dissolved in methanol and added to 50 ml of oxalic acid (0.5 M) in water at 5°C
CaC_2O_4 in CH_3OH RT	As above the preparation temperature was at room temperature

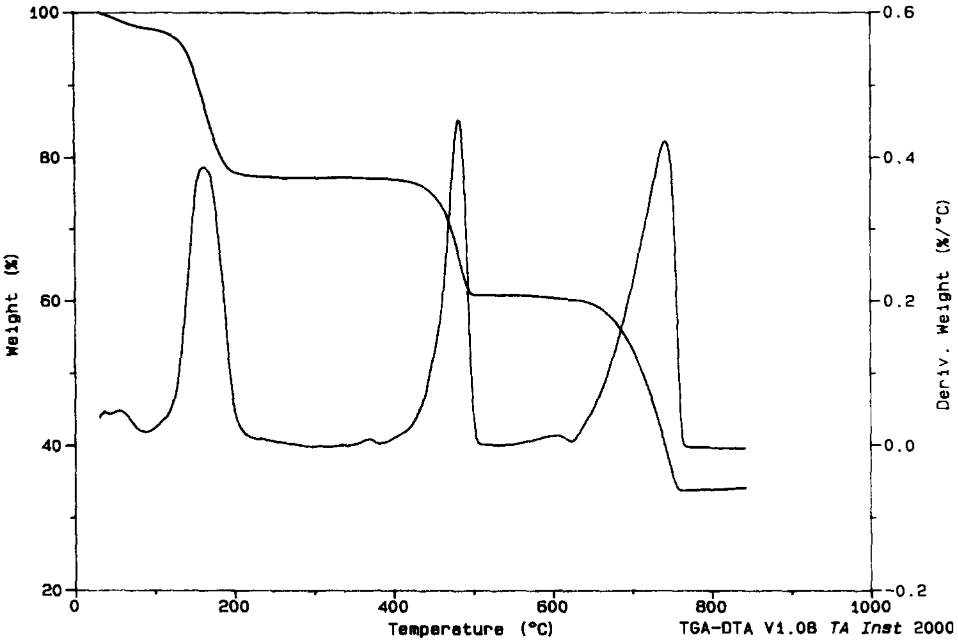

Fig. 1. TG/DTG plot for sample CaC_2O_4 (commercial).

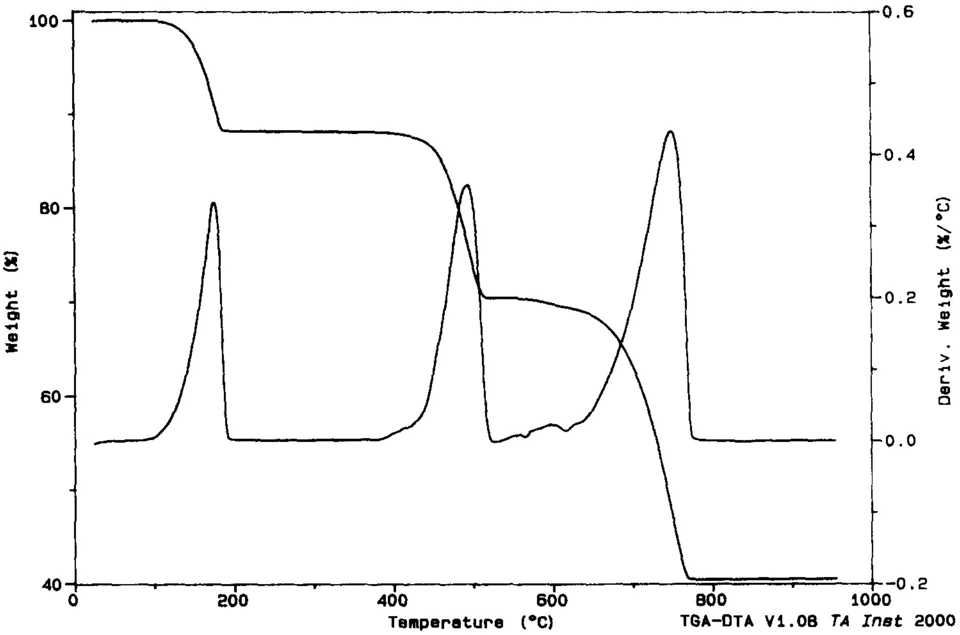

Fig. 2. TG/DTG plot for sample CaC_2O_4 (0.75 M) 5°C.

Table 3
Summary of the compositional changes and the temperature of the stage for decomposition of calcium oxalate samples

Sample	Dehydration		Decomposition to $CaCO_3$		Decomposition of $CaCO_3$	
	% mass residue	Peak temp. DTG/C°	% mass residue	Peak temp. DTG/C°	% mass residue	Peak temp. DTG/C°
CaC_2O_4 (comm.)	88.0	177.9	70.3	492.8	40.4	750.0
CaC_2O_4 (0.75 M) 0	76.0	180.3	59.4	485.6	34.4	754.8
CaC_2O_4 (0.75 M) 5	77.1	163.5	60.8	485.6	33.7	742.8
CaC_2O_4 (0.75 M) RT	78.6	182.7	62.8	485.6	34.8	762.0
CaC_2O_4 (0.75 M) 70	87.2	163.5	70.1	468.8	40.4	726.0
CaC_2O_4 (1.5 M) 5	74.1	180.2	56.1	485.6	27.3	759.6
CaC_2O_4 (1.75 M) 5	85.5	185.1	66.7	495.2	36.4	774.0
CaC_2O_4 in CH_3OH 5	86.2	177.9	68.0	459.1	39.4	762.0
CaC_2O_4 in CH_3OH RT	87.4	161.1	70.4	468.8	41.0	726.0

(0.75 M) RT giving patterns which could be identified as the dihydrate. The CaC_2O_4 (1.5 M) 5°C also gave an X-ray diffraction pattern corresponding to the dihydrate but it has been noted that the TG data is more complicated due, it is thought, to an inability to remove all the urea, despite the continued washing of the precipitate.

Each stage in the decomposition was analyzed to establish the kinetic parameters using the method of selecting the mechanism advocated by Dollimore et al. [6]. A first-order reaction mechanism gave the best fit overall for all the samples investigated for each stage of the decomposition mechanism – that is, dehydration – decomposition of the oxalate to carbonate. For the purpose of comparison, therefore, a first-order kinetic analysis is reported on all the samples at every stage. A derivative method was used [7], where the rate of reaction ($d\alpha/dt$) is given by

$$d\alpha/dt = k(1-\alpha)$$

for a first-order mechanism where α is the fraction decomposed (in the step being considered), k is the specific reaction rate, and t is the time.

The data from the $\alpha - T$ curve gives $d\alpha/dt$ at various values of α and T, when

$$d\alpha/dt = \frac{d\alpha}{dT} \cdot \beta$$

where β is the heating rate, and $k = (d\alpha/dt)\beta/(1-\alpha)$ and this can be substituted into the Arrhenius equation to give

$$\ln \frac{d\alpha}{dT} \cdot \beta/(1-\alpha) = \ln A - E/RT$$

where A is the pre-exponential factor and E is the activation energy. A plot of $\log(d\alpha/dT)\beta/(1-\alpha)$ vs. $1/T$ gives A and E. A typical plot of this kind is shown in Fig. 3. The kinetic parameters established by the above procedure are summarized on Table 4.

The dehydration stage is thus seen to be characterized by large values of E for the monohydrate and lower values of E for the dihydrate. There is some correlation with the temperature of preparation in that the dihydrate is favored by low temperature preparative conditions. Correlation with E for the oxalate to carbonate stage is not apparent. The final stage decomposition of the carbonate also shows no correlation with either the original composition or any other detail

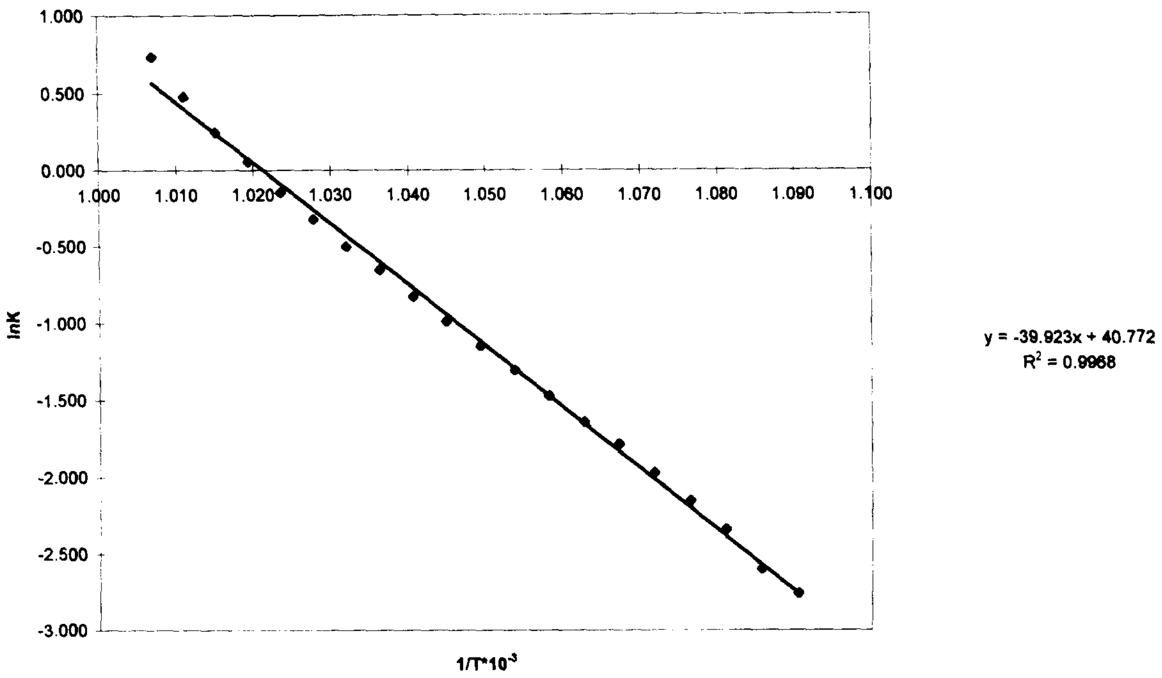

Fig. 3. Typical Arrhenius plot, for CaC_2O_4 in methanol, RT data for calcium carbonate decomposition stage.

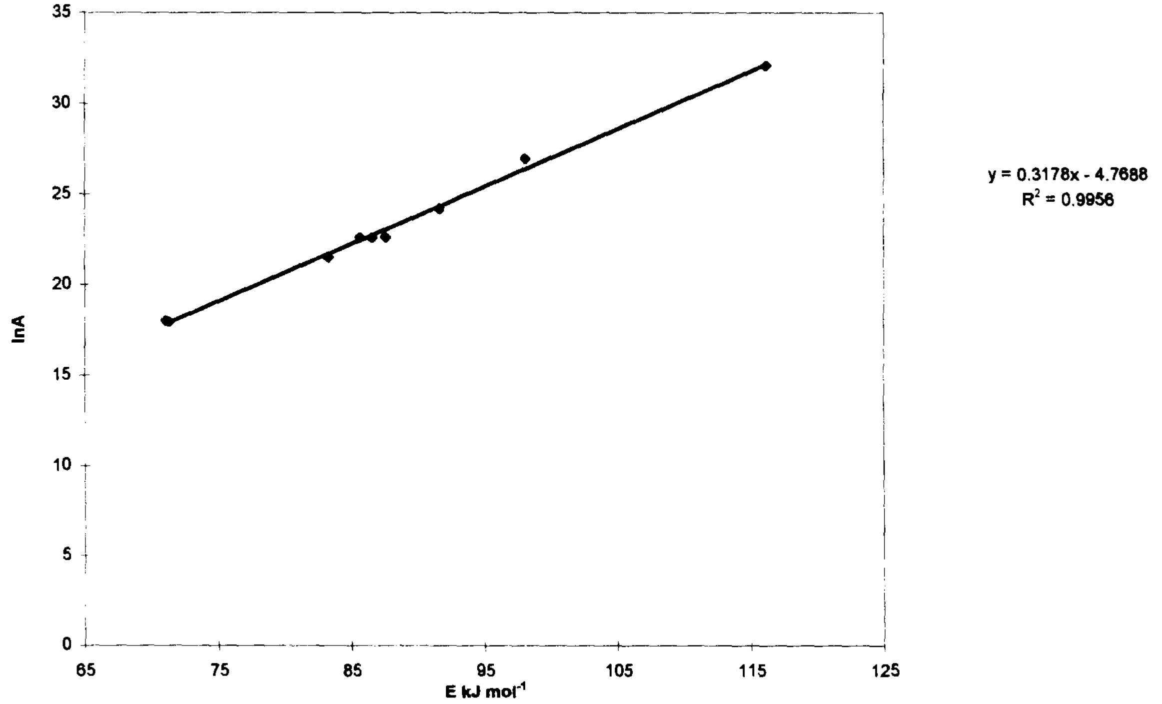

Fig. 4. Compensation plot of ln A against E for the dehydration stage.

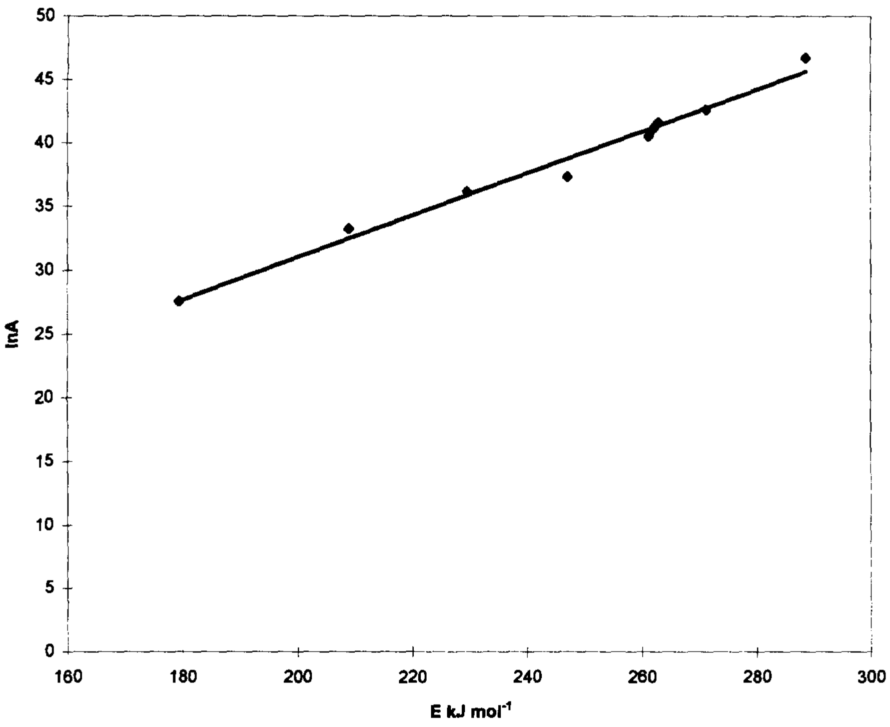

Fig. 5. Compensation plot of ln *A* against *E* for decomposition of the oxalate to carbonate.

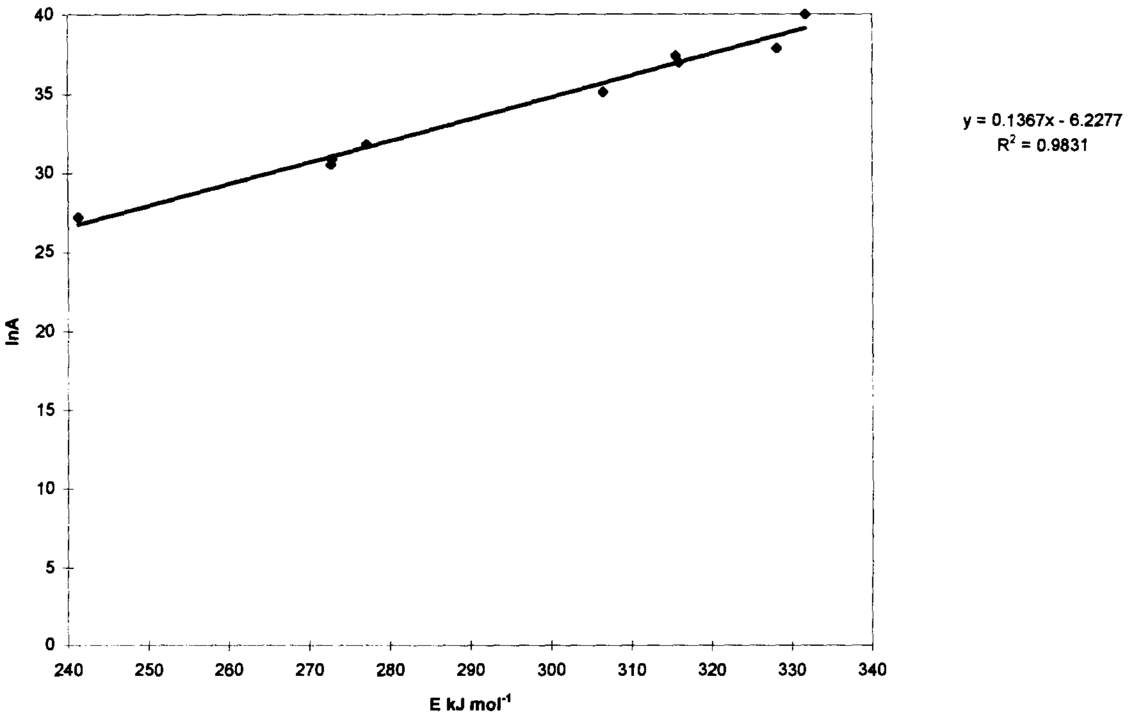

Fig. 6. Compensation plot of ln *A* against *E* for the carbonate decomposition stage.

of the preparative conditions. This is probably because marked compensation effects exist between ln A and E at all stages of decomposition [8]. The compensation effect is shown in Figs. 4–6 for all three of the decomposition processes.

4. Summary

The preparation of calcium oxalate dihydrate needs air drying of the precipitate as drying in a conventional oven at 100°C drives off the extra water molecule and results in the formation of the monohydrate.

Air drying of calcium oxalate prepared in the presence of urea at concentrations of urea up to 1.5 M, and at temperatures below 25°C resulted in the formation of the dihydrate. The precipitates from the methanol solutions were of the monohydrate form of calcium oxalate. The energy of activation for the dehydration stage showed high values for the monohydrate and lower values for the dihydrate.

All three oxalate decomposition stages – the dehydration, the decomposition to the carbonate and the decomposition of the carbonate – were amenable to a first-order reaction mechanism and showed a compensation effect for each decomposition stage.

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