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Thermochimica Acta 357–358 (2000) 79–87

thermochimica
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A study of the decomposition of calcium propionate, using simultaneous TG-DTA

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Received 15 September 1998; accepted 22 August 1999

Abstract

Chemical preservatives are added to almost all foods to prevent spoilage and extend the shelf life, by inhibiting the growth and metabolic activity of microbes. Since most foods are subjected to heating, either by the consumer or by the manufacturer, the thermal behavior of a preservative is very important. In this study, the decomposition of calcium propionate was examined using simultaneous TG-DTA, with a rising temperature program and heating in dry nitrogen and air. The material initially decomposed to $CaCO_3$, and then to CaO with further heating. The process was endothermic in nitrogen, but exothermic in air. Scanning electron microscopy (SEM) and powder diffraction was used to confirm the thermal analysis data. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calcium propionate; Thermal analysis; Preservatives; Decomposition; Powder diffraction; Food science

1. Introduction

The use of food preservatives is becoming increasingly more common as the demand for foods with extended shelf life increases. Preservatives are necessary since most foods are grown, processed and marketed in different regions, allowing several days or weeks to pass before the product is consumed. Chemical preservatives are substances added to products to prevent or decrease the growth of microbes, including bacteria, yeast and molds, which thrive in the moderate pH and temperature of foods. Most foods contain a combination of two or more chemical preservatives for maximum antimicrobial effect. Chemical preservatives are also found in pharmaceuticals, cosmetics and personal care items.

In previous studies, the thermal decomposition of benzoic, sorbic and citric acids, which are common preservatives, were determined using thermal analysis [1]. The thermal behavior of another frequently used preservative, calcium propionate, is described in this paper. Calcium propionate, the calcium salt of propionic acid, is a fine, white powder. It is slightly effective against spore-forming bacteria, such as *Bacillus subtilis*, a type of bacteria that causes bread to spoil [2]. It is most effective against molds at pH values less than 5 or 6, depending on the type of food [3]. Calcium propionate causes little inhibition of yeasts, so it can be used in breads and other baked goods that require leavening. The antimicrobial activity of the propionates results from the interference of the electrochemical gradients of the cell membrane, which disrupt transport processes [2]. The uptake of substrate molecules, such as phosphate and amino acids, is also inhibited. Calcium propionate is used to preserve products such as bread, cheese and baked goods.

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PII: S0040-6031(00)00371-3

2. Materials and methods

The anhydrous calcium propionate [$(C_2H_5CO_2)_2Ca$] was obtained from Aldrich, 97% purity, CAS No. 44075-81-4. The thermal analysis equipment consisted of a simultaneous TG-DTA unit, TA Instruments Model No. 2960. The experimental data was analyzed with TA Instruments Universal Analysis software, V1.10B. The samples were heated in both dry nitrogen and dry air at a flow rate of 100 ml min^{-1}, in a platinum crucible with an empty platinum crucible as a reference. The gas flow rate was monitored with an electronic flowmeter. The heating rate (β) was 10°C min^{-1} to 1000°C. In order to exclude error, three runs were completed with each purge gas. Plots of weight percentage, derivative weight and temperature difference against temperature and time were obtained. All endothermic and exothermic temperatures were peak temperatures.

A powder diffraction pattern was obtained using the Scintag XDS 2000, mounted on a X-ray generator, operating at the Cu Kα wavelength (1.5406 Å), 45 kV and 40 mA. The projecting slits were 2 and 4 on the X-ray tube. The receiving slits were 1 on the front and 0.2 on the back. The sample was scanned from 8.000 to 40.00θ, with a scan rate of 2.00 and a chopper increment of 0.030. The material was firmly pressed into an aluminum sample holder, with an area of 30 mm by 30 mm. The experimental pattern was compared with patterns obtained from the JCPDS database.

The morphology of calcium propionate was also viewed with the scanning electron microscope (SEM). The first sample contained pure, untreated calcium propionate. The second sample was heated to 500°C in dry nitrogen, using the thermal analysis instrument. The samples were sprinkled onto carbon conductive tape that was attached to aluminum sample stubs and then sputter coated with a gold/palladium cathode for 25 s. The JEOL JSM 6100 SEM was used to visualize the samples at an accelerating potential of 5.0 kV. The entire sample was scanned and a representative

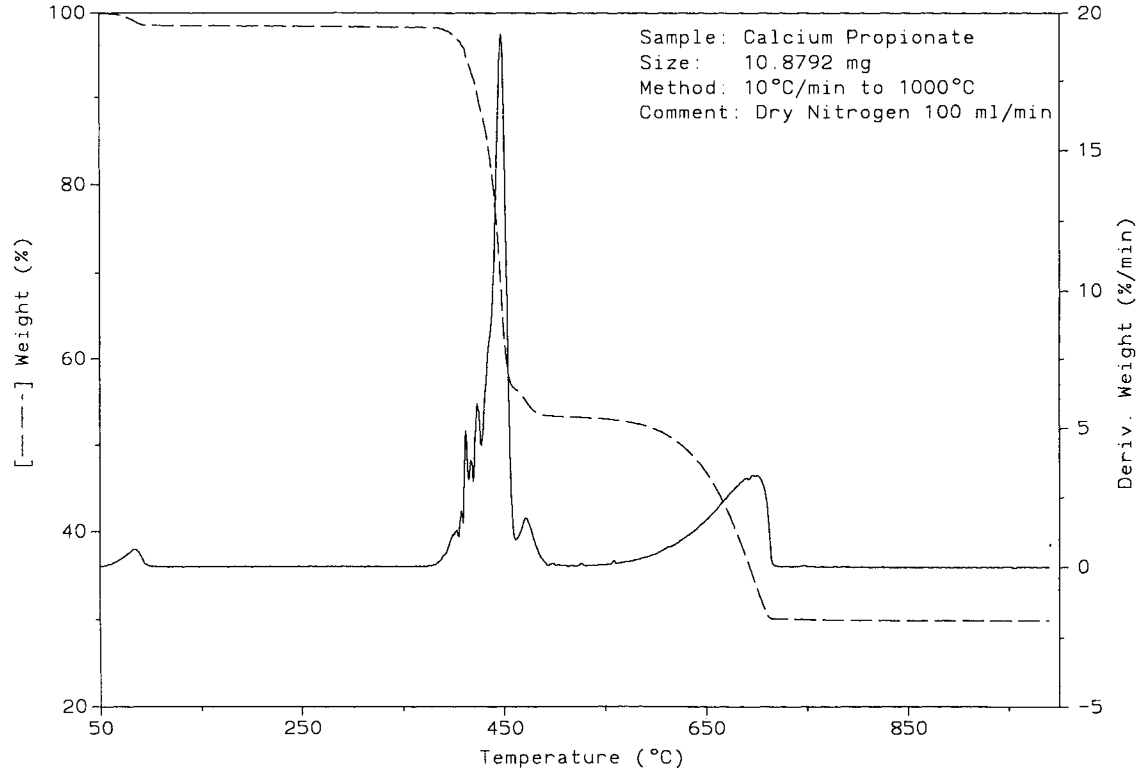

Fig. 1. TGA-DTG plot of calcium propionate heated 10°C min^{-1} in dry nitrogen.

photograph was taken at a magnification of ×2000 with Polaroid 52 film.

3. Results

3.1. Calcium propionate heated in nitrogen

When the calcium propionate was heated in dry nitrogen, the TGA plot of weight percentage versus temperature contained three regions of mass loss, as presented in Fig. 1. Although the compound was sold as anhydrous, a 1.5% mass loss was observed by 100°C, corresponding to the loss of water. The samples were taken from a freshly opened container, placed in the sample crucible and analyzed immediately, as calcium propionate is very hygroscopic. After drying, the sample consisted of pure calcium propionate. The mass remained stable until 400°C, when it rapidly decreased, as the material decomposed, most likely to $CaCO_3$, CH_4 and CO. An average of 53.0% of the initial mass remained at 524°C, which is equivalent to the theoretical mass of 53.7% attributed to calcium carbonate. The mass stabilized until 600°C, when it decreased as the residue further decomposed to calcium oxide. At 749°C, an average of 29.8% of the initial mass was present as a white powder, corresponding to a theoretical mass of 30.1%, attributed to calcium oxide. After about 450°C, the TGA curve appears similar to the TGA curve of $CaCO_3$.

Fig. 2, contained a small mass loss of 1.5% before 96°C, resulting from the loss of absorbed water. The mass stabilized between 96.3 and 288.3°C, when the sample consisted of pure calcium propionate. After 288°C, the mass declined rapidly. An unstable intermediate formed around 385°C, which decomposed by 439.0°C. The mass stabilized again between 507.3 and 580.4°C. At 500°C, 52.7% of the initial mass remained, corresponding to the theoretical mass of

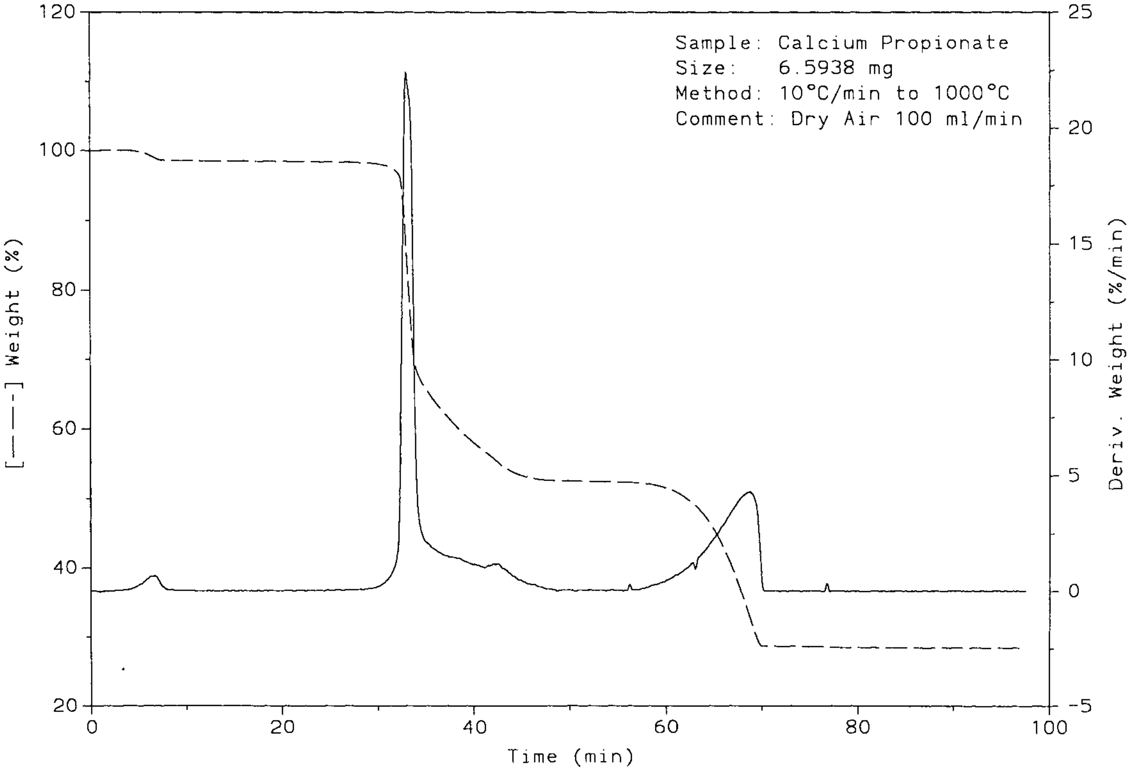

Fig. 2. Plot of weight percentage and derivative weight versus time for calcium propionate heated 10°C min^{-1} in dry air.

53.7% attributed to $CaCO_3$. After that temperature, the mass decreased significantly and then stabilized again after 709.8°C. At the end of the runs, 28.5% of the initial mass remained as CaO.

The DTG plot, which is presented in Fig. 2, contained four peaks. A small peak at 83.1°C, with an average peak rate of mass loss of 0.05227 mg min^{-1}, was the result of water loss. A large, asymmetrical peak was observed at an average temperature of 387.7°C. The mean peak rate of mass loss was 1.654 mg min^{-1}. This peak was the result of the primary decomposition of calcium propionate and was followed by a small, poorly resolved peak resulting from the decomposition of the unstable intermediate. A broad peak, with average maximum d*m*/d*t* of 0.3414 mg min^{-1}, was observed at a mean temperature of 706.3°C as the final decomposition took place.

The DTA plot of temperature difference against temperature is shown in Fig. 3. A small endotherm is observed at 84.9°C, resulting from water loss. A large exotherm, which slopes towards the right, is observed at an average temperature of 403.0°C. The extent of this exotherm is so great that it alters the rate of heating, altering the temperature scale, as shown in the plot of temperature versus time in Fig. 4. Therefore, the curves of weight percentage and derivative associated with a mass loss, indicating that it is also the result of a crystal transi-tion or phase change. Endotherm 4 was followed by a series of small, narrow, asymmetrical peaks. The peaks were poorly resolved and the number varied from sample to sample, due to lack of resolution. The series of peaks was followed by a broad, shallow, poorly resolved peak at an average peak temperature of 511.4°C. This group of peaks is the result of decomposition with the evolution of CO and CH_4, leaving the intermediate compound, calcium carbonate. The final and largest endotherm is seen at an average temperature of 698.8°C. It is the result of the decarboxylation of calcium carbonate to calcium oxide, which is an endothermic process. The

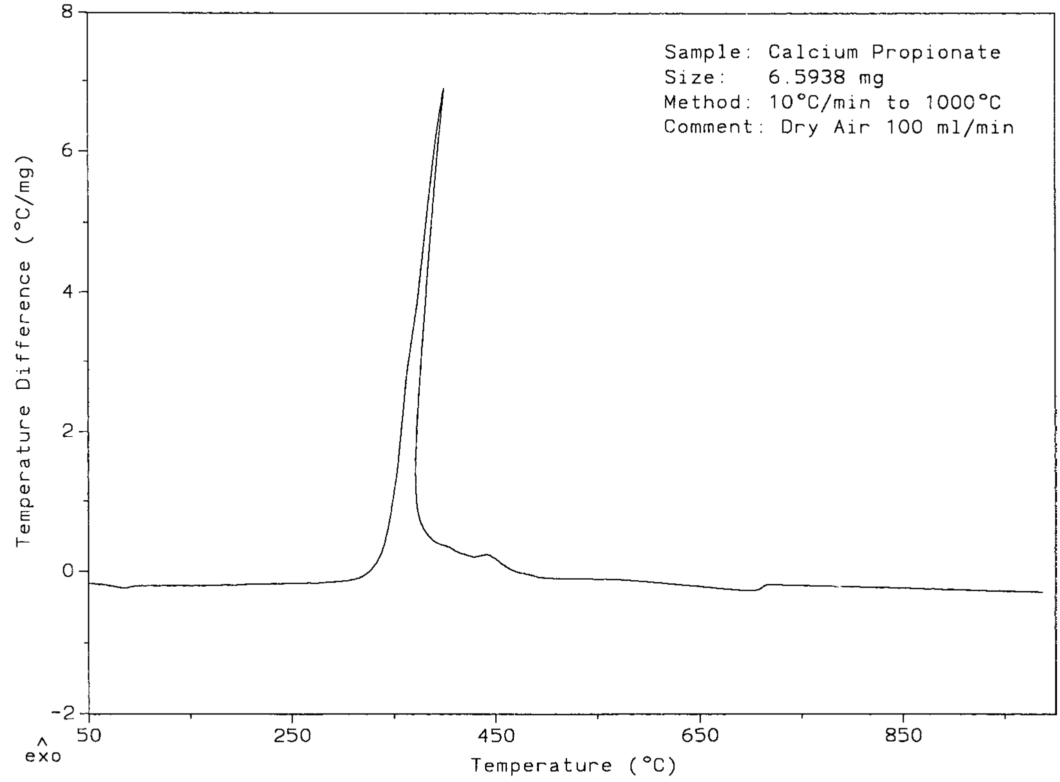

Fig. 3. Plot of temperature difference versus temperature for calcium propionate, heated 10°C min^{-1} in dry air.

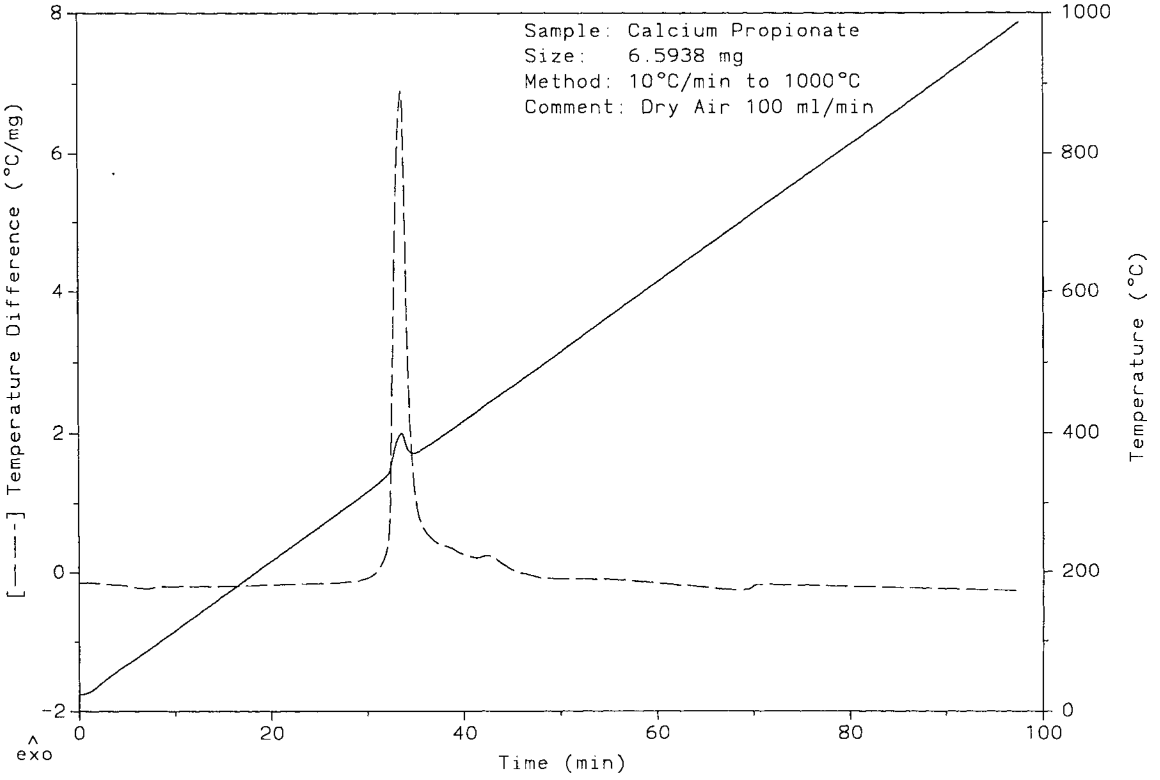

Fig. 4. Plot of temperature and temperature difference versus time for calcium propionate.

endotherm is observed at the same temperature as pure calcium carbonate.

To assess for reversibility, a pair of runs was completed by heating a sample of calcium propionate at a rate of 10°C min^{-1} to 395°C. The sample was allowed to slowly cool to ambient temperature and was then heated 10°C min^{-1} to 1000°C. The DTA plot can be found in Fig. 5. The endotherm corresponding to drying was not observed in the second run, confirming its identity. Endotherm 2 was not observed in the second run, indicating that a non-reversible transition occurred. A reversible transition occurred at 269.5°C, since a peak was observed at that temperature in both runs. Endotherm 4 was also the result of a reversible transition, since it was found in both runs at the same temperature.

3.2. Calcium propionate heated in air

When the purge gas was changed to dry air, the decomposition of calcium propionate occurred via a different mechanism. The TGA plot of weight percentage versus time, which is shown in the DTG plot of derivative weight versus temperature contained four peaks of various shapes and areas, as shown in Fig. 1. The first peak, which was symmetrical and the smallest of the four peaks, was observed at a mean temperature of 83.7°C. It results from the loss of absorbed water. The second peak was observed at an average temperature of 448.8°C. It was sharp, asymmetrical and the largest of the DTG peaks. As can be observed in Fig. 1, all runs in nitrogen contained a series of small, irregular spikes on the DTG plot, just prior to the main peak, indicating that the rate of mass loss rapidly oscillated before the main decomposition. Immediately after the large peak, another small peak, which was sharp and fairly narrow, was observed at about 472.7°C. The DTG data suggests that calcium propionate decomposes to an intermediate compound in at least two or more steps. The intermediate compound then decomposes at a higher temperature. The peak at 697.4°C, representing the final decomposition,

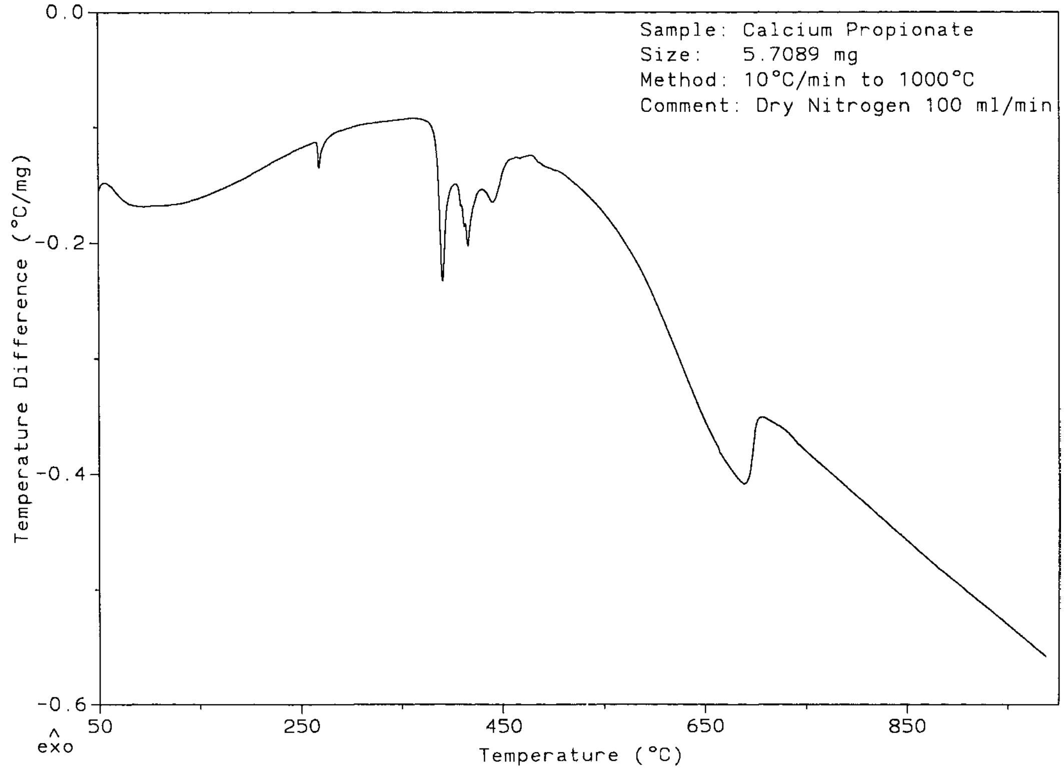

Fig. 5. DTA plot of calcium propionate after heating to 395°C and cooling.

was broad and asymmetrical, with fronting. The maximum rates of mass loss (d*m*/d*t*) are summarized in Table 1.

Table 1
Experimental d*m*/d*t* values for calcium propionate heated in dry nitrogen

Temperature (°C)	d*m*/d*t* (mg min^{-1})
Sample 1	
83.71	0.0583
452.62	2.066
474.32	0.1596
691.33	0.2886
Sample 2	
83.78	0.0583
446.84	2.094
471.88	0.1873
699.32	0.3531
Sample 3	
83.78	0.0503
446.84	1.383
471.88	0.1301
701.41	0.2898

The DTA plot, which is presented in Fig. 6, contained several endothermic events. The experimental data is summarized in Table 2. The first endotherm, which was sharp, narrow and fairly symmetrical, had an average peak temperature of 87.7°C. This peak corresponds to the loss of water. Two small, closely spaced endotherms were observed at average temperatures of 224.4 and 272.5°C. A sharper, better-resolved peak, designated Endotherm 3, followed Endotherm 2, which was broad and poorly resolved. These endotherms were not accompanied by a mass loss, eliminating decomposition as the source of the peaks. They are the result of a crystal or other phase transition. Endotherm 4, which was very narrow, large and sharp, was observed at a consistent peak temperature of 392.6°C, in all runs. This endotherm was not weight are plotted against time, since the curves appear distorted when plotted against temperature, as shown in Fig. 7. When temperature difference versus time is plotted, the exotherm no longer slopes to the right, as presented in Fig. 4. Two smaller exotherms are

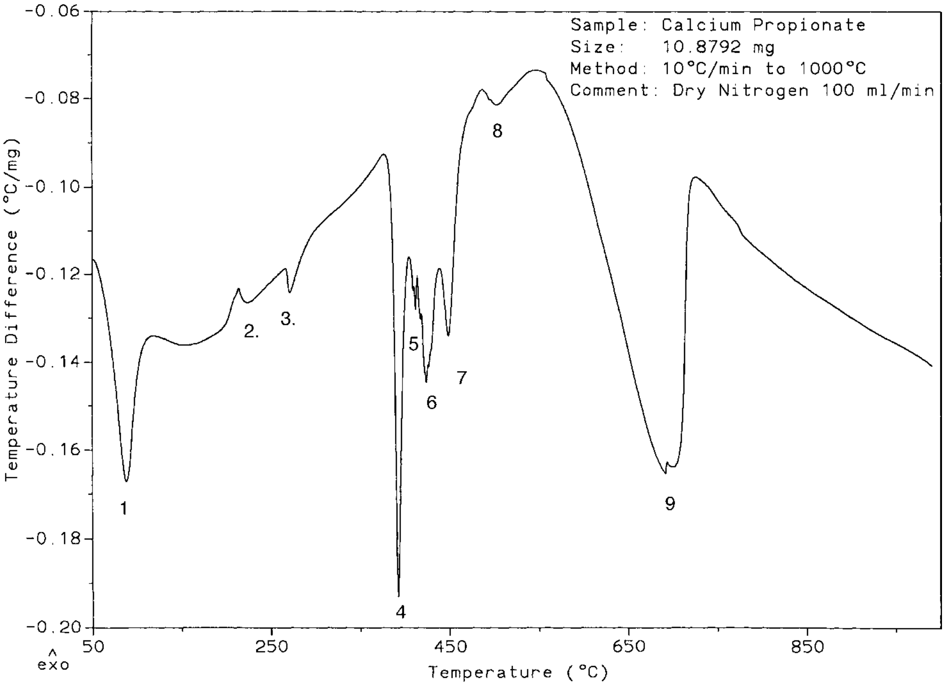

Fig. 6. DTA plot of calcium propionate heated 10°C min^{-1} in dry nitrogen.

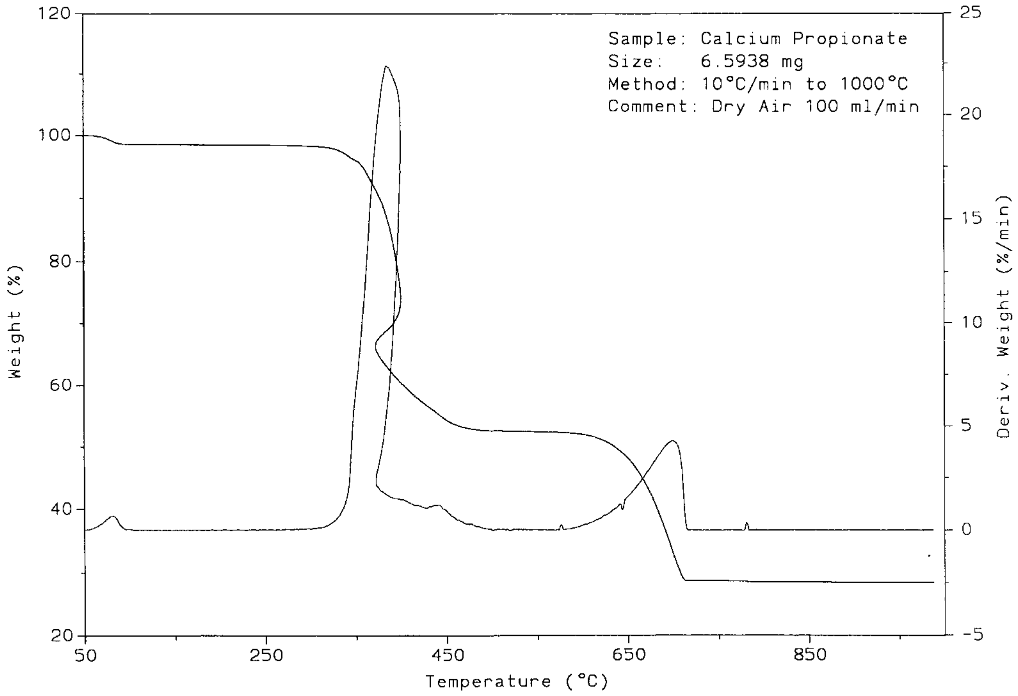

Fig. 7. Plot of weight percentage and derivative weight versus temperature for calcium propionate heated 10°C min^{-1} in dry air.

Table 2
DTA results for calcium propionate in N_2[a]

Sample	E_1 (°C)	E_2 (°C)	E_3 (°C)	E_4 (°C)	E_5 (°C)	E_6 (°C)	E_7 (°C)	E_8 (°C)	E_9 (°C)
1	87.05	223.93	272.34	392.53	415.90	429.25	454.29	527.74	699.68
2	87.95	223.58	271.57	392.59	412.88	423.89	448.93	503.18	693.06
3	87.95	225.67	273.66	392.59	413.46	421.80	448.93	503.18	703.50
Mean	87.65	224.39	272.52	392.57	414.08	424.98	450.72	511.37	698.75

[a] Endothermic temperatures are peak temperatures.

observed at 439.0 and 697.1°C, resulting from the decomposition of the intermediate to $CaCO_3$ and the formation of CaO, respectively.

3.3. Powder pattern of calcium propionate

The powder pattern of calcium propionate is presented in Fig. 8. The pattern consisted of three sharp peaks between 7θ and 10θ, followed by many smaller peaks, indicating a fairly crystalline material. Three powder patterns were obtained from the database. The experimental pattern contains a large peak at 7θ, which is found only in the monohydrate pattern from the database, indicating that the sample actually contains some monohydrate. The sample is a mixture of anhydrous and monohydrate calcium propionate,

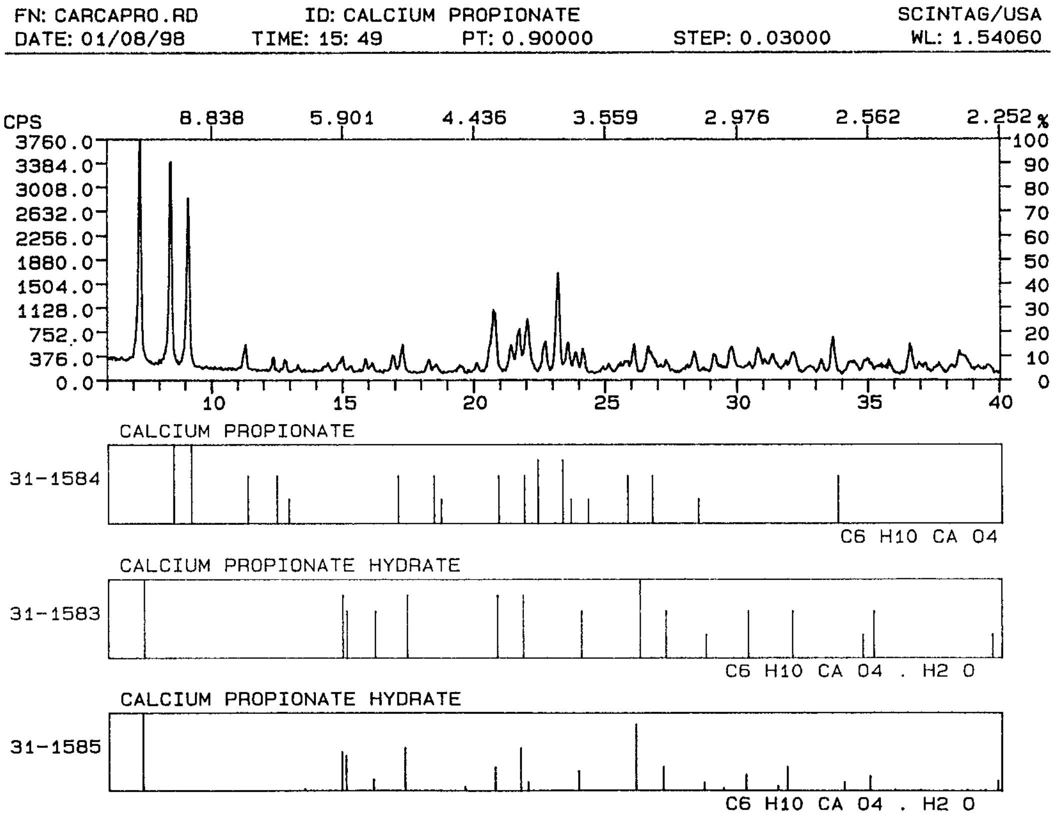

Fig. 8. Powder diffraction pattern of calcium propionate.

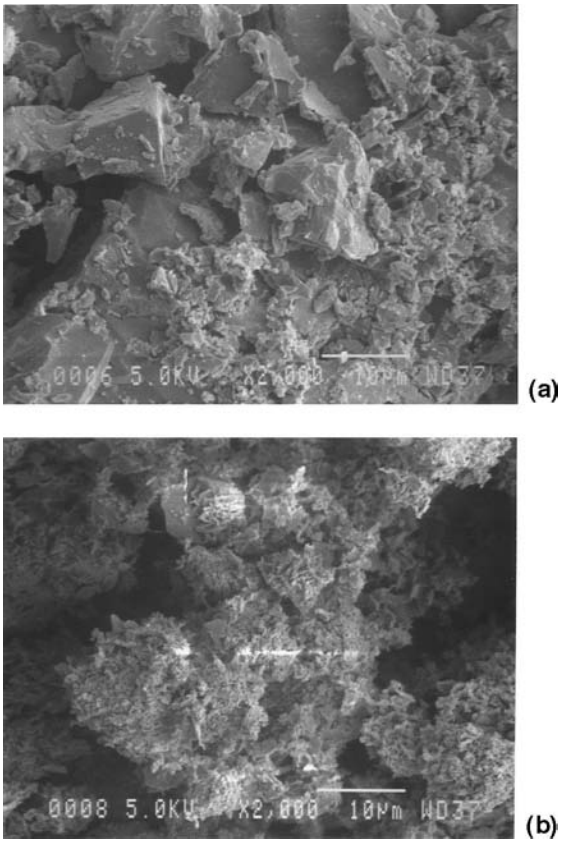

Fig. 9. SEM photographs of calcium propionate before (a) and after heating to 500°C (b).

as peaks at 8 and 9θ are observed. These peaks are only seen on the anhydrous data base pattern. This data confirms the TGA data that suggested the initial water loss.

3.4. Scanning electron microscopy

A sample of calcium propionate was viewed with the scanning electron microscope at 2000× magnification. The sample consisted of irregularly shaped, rough particles, approximately 10 μm in diameter, as shown in Fig. 9a. Small fragments of material were also observed. The sample that had been heated to 500°C was also examined Fig. 9b. The sample was heated to the temperature past the conversion to $CaCO_3$, as shown on the TGA plot. The particle size is much smaller and the surface area is greatly increased, confirming that the heating changed the chemical composition.

4. Conclusions

It can be concluded that calcium propionate decomposed to an unstable intermediate via an exothermic process in air. The intermediate then decomposed to calcium carbonate with further heating. The decomposition occurs via endothermic processes in an inert atmosphere, such as nitrogen. Thermal analysis provides an effective method to evaluate the hydration and purity of these compounds, as well as the thermal stability.

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