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# The origin of the exothermic peak in the thermal decomposition of basic magnesium carbonate

N. Khan, D. Dollimore[†], K. Alexander[*], F.W. Wilburn

*Department of Industrial Pharmacy and Department of Chemistry, University of Toledo, Toledo, OH 43606, USA*

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## Abstract

The thermal analysis of basic magnesium carbonate has been investigated by thermogravimetry (TGA), derivative thermogravimetry (DTGA) and differential thermal analysis (DTA). The end product was magnesium oxide formed from the decomposition of magnesium carbonate. The composition of the samples studied varied, but the general formula that represented them was $x\mathrm{MgCO_3}\cdot y\mathrm{Mg(OH)_2}\cdot z\mathrm{H_2O}$. In the present study, the thermal analysis of such magnesium carbonates in nitrogen, carbon dioxide and air was carried out at different heating rates and the origin of the exothermic peak was studied. Generally, the decomposition peaks were endothermic, but a persistent exothermic peak was noted, always accompanied by a very sharp drop in the TG curve, and the weight loss in this region may be significant. The exothermic DTA peak was found to be strongly influenced by the rate at which the samples were heated, sample size and atmospheric conditions. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Magnesium carbonate; DTA; TG; Exothermic peak; XRD; SEM

## 1. Introduction

Magnesium carbonate is an inorganic compound used in combination with other hydroxides and carbonate compounds and sometimes alone in antacid formulations. It is formulated in tablet form and as an aqueous suspension [1].

Magnesium carbonate is described as a light, white, amorphous, odorless and tasteless powder, capable of absorbing odors readily. It is stable in air and slowly absorbs carbon dioxide on exposure to air. The decomposition temperature of magnesium carbonate is quoted as 230–680°C. It is practically insoluble in water and alcohol and readily soluble in dilute acid. In water containing carbon dioxide, it forms magnesium bicarbonate, which is soluble in water [1].

$$\mathrm{MgCO_3 + H_2O + CO_2 \rightarrow Mg(HCO_3)_2}$$

There are two pharmaceutical varieties of magnesium carbonate; namely, light and heavy which are best regarded as conforming to the general formula, $x\mathrm{MgCO_3}\cdot y\mathrm{Mg(OH)_2}\cdot z\mathrm{H_2O}$. The light form, which is 2–2.5 times as bulky as the heavy, is most commonly used in the pharmaceutical industries.

The light and heavy magnesium carbonates can be prepared by various routes [3–7]. Typically by mixing a solution of magnesium sulfate or chloride with sodium carbonate solution. Precipitation in cold solution gives a very bulky precipitate which dries to a voluminous light powder, called *magnesia alba levis* or the light form ($\mathrm{3MgCO_3\cdot Mg(OH)_2\cdot 3H_2O}$), while precipitation in a boiling solution gives a denser form

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[*] Corresponding author.

*E-mail address*: kalexan@utnet.utoledo.edu (K. Alexander).

[†] Deceased

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called *magnesia alba ponderosa* or heavy powder ($3MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$). The light form can also be prepared from dolomite ($MgCO_3 \cdot CaCO_3$). Dolomite is first calcinated, the calcined product is suspended in water and saturated with carbon dioxide under pressure. On increasing the temperature, the lime precipitates as insoluble carbonate. The filtered solution is then heated to the boiling temperature whereupon magnesium bicarbonate loses carbon dioxide and water and magnesium carbonate is collected as a precipitate [1].

Magnesium carbonate in nature exists as a geological material called magnesite, which is the anhydrous carbonate, $MgCO_3$. Magnesite undergoes decomposition on heating to give magnesium oxide and carbon dioxide [8,9]

$$MgCO_3 \rightarrow MgO + CO_2$$

In the present study, the thermal decomposition of magnesium carbonate was studied by thermogravimetry (TGA), derivative thermogravimetry (DTGA) and differential thermal analysis (DTA). Decomposition of the basic magnesium carbonate was studied by plotting percentage weight against temperature (TGA curve). The DTA has been used as the main technique to study the origin of the exothermic peak.

The decomposition reported in preliminary studies in this laboratory in nitrogen at 10°C/min shows the reaction occurring in at least two stages, each endothermic, and in two temperature ranges. The degradation shows a loss of moisture followed by the loss of carbon dioxide and hydroxyl water. The appearance of an exothermic peak in an atmosphere of carbon dioxide has been reported earlier [3,10]. However, the information on the effect of the experimental parameters on this peak is limited [2].

The present study reveals the influence of heating rate, sample size and atmospheric conditions on the origin of exothermic peak.

## 2. Materials and equipment

The materials used in the study can be described as light magnesium carbonate USP (lot # 886814) manufactured by Fisher Scientific.

The thermogravimetry unit TA instrument SDT 2960 with simultaneous DTA was used to carry out the thermal analysis. It has three major components; sample and reference balance assemblies with platinum–platinum/13% Rhodium thermocouples; a furnace with electronic control of sample atmosphere and temperature; and a workstation where electronic and mechanical systems are housed.

TGA, DTA and DTGA plots of the samples were obtained:

1. At different rising temperatures of 10, 15, 18, 18.5, 19, 20 and 25°C/min up to a temperature of 950°C.
2. At different sample sizes of 6–10 and 15–18 mg with varying heating rates.
3. At varying atmospheric conditions of dry nitrogen, dry carbon dioxide and dry air.

The platinum crucibles were used to hold the sample and an empty platinum crucible was used as the reference standard. The temperature range studied was from 30 to 950°C.

The solid products of decomposition were prepared by firing the light magnesium carbonate in a tube furnace at different temperatures of 522 and 574°C in dry nitrogen and at 520°C in dry carbon dioxide, until the weight loss was similar to that obtained from the TGA plot (approximately 2 h in each instance).

The samples were subjected to scanning electron microscopy (SEM) using a JOEL JSM-6100. To make the sample conductive, the sample was coated with a gold coating by using a Denton Desk II sputter coater that was operated under a condition of 50 mTorr. The current for coating was 45 mA and the coating time was 25 s. The SEM working accelerating voltage was 10 kV with a working distance of 29–39 mm.

The initial composition of the sample was studied using an X-ray diffraction (XRD) unit, XDS 2000 SCINTAG INC. The initial phase of the samples was found to correspond to $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ from XRD. The XRD paved the way for calculating the composition of the sample, which was found to be $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. During thermal analysis, the sample will be expected to undergo the following decomposition pattern: loss of adsorbed water; loss of water of crystallization; and decomposition of carbonate and hydroxy entities, in that order as the temperature is increased.

## 3. Results and discussions

The thermal analysis curves for the different samples (light magnesium carbonate and basic heavy magnesium carbonate) did not show any marked differences at similar experimental conditions but did indicate that the samples were not simply magnesium carbonate. This was proven by XRD, which showed that the samples were actually magnesium carbonate hydroxide hydrate identified as hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$). From the weight loss, the composition of the sample was found to be $3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$. From the DTA (Table 1), DTA and TGA (Figs. 1 and 2), following observation were made. The absorbed water was lost below or near 100°C. The DTGA and endothermic peak between 130 and 350°C were due to loss of water of crystallization. The DTGA and highly endothermic peak between 306 and 520°C were attributed to the loss of hydroxyl water and carbon dioxide. From all the tables and figures, it can be observed that depending upon the experimental parameters, an exothermic DTA peak was observed in the range of 520–530°C. In an atmosphere of carbon dioxide, a fourth DTGA peak was observed due to the loss of carbon dioxide.

Earlier studies show the presence of an exothermic peak [3,10]. In the present study, the influence of the heating rate, sample size and atmospheric conditions on the exothermic peak were studied.

### 3.1. Effect of heating rate

Fig. 1 shows a typical DTA curve in dry nitrogen purge gas for the thermal decomposition of light magnesium carbonate supplied by Fisher Scientific. The DTA curve shows two or three endotherms. In certain cases, after the second endotherm, a very sharp exotherm was recorded immediately followed by the third endotherm. The results have been found to be similar to that of the basic heavy magnesium carbonate at similar conditions. Table 2 summarizes the results obtained at different heating rates (sample size 6–8 mg) in an atmosphere of dry nitrogen and at a flow rate of 50 ml/min. From the figure and table, the following observations can be made.

When the thermal analysis of the sample was carried out at a slow heating rate of 10, 15 and 18°C/min, then two endothermic peaks were observed and no exothermic peak was observed. From the TGA curve, the first endothermic peak was due to the loss of water of crystallization. The second endothermic peak was due to the loss of hydroxyl water and loss of carbon dioxide from magnesium hydroxide and magnesium carbonate respectively. When the heating rate was increased to 18.5°C/min, then an exothermic peak was observed around 525.35°C. The area/size of the exothermic peak increased, as the heating rate was further increased. It was also observed that the peaks appear at slightly higher temperature with increasing heating rate and the effect was not attributed to the instrument as it was calibrated at each heating rate.

Fig. 2 shows a typical TGA curve for the light magnesium carbonate sample in dry nitrogen, sample size 6–8 mg. The results of different heating rates have been summarized in Table 1. From the table, it can be observed that at 18.5°C/min, a spiked peak was produced at 528°C, immediately following the second DTG peak. As the heating rate was increased, an increase in the area/size of the spiked peak was observed. The percentage weight of the MgO produced at the end of the reaction in all the experiments was approximately 44%. The appearance of the exotherm shows that increasing the heating rate produces a stress in the sample that is released as heat.

### 3.2. Effect of sample size

Fig. 3 shows the influence of sample size on the exothermic peak in the DTA plot. The results have been summarized in Table 3. When the size of the sample in the crucible was increased to 15–18 from 6 to 8 mg, an exothermic peak was observed, even at a slow heating rate of 15°C/min. An exothermic peak has been reported by Choudhary and Pataskar at 10°C/min with a sample size of 30 mg [11].

The detailed TG/DTG of the sample in dry nitrogen, sample size 15–18 mg is summarized in Table 4 and Fig. 4. From the table and the TG curve, a dramatic decrease in the percentage weight was observed when the exotherm occurred. The difference in initial weight and final weight ($\Delta W$) increased, with an increase in heating rate. It was also observed that the area of the second DTG peak decreased with increasing heating rate.

Table 1
TG/DTG data for runs in dry $N_2$ (flow rate 50 ml/min) for an initial mass of 6–8 mg for the light magnesium carbonate sample supplied by Fisher Scientific (lot # 886814)

| Heating rates (°C/min) | First DTG peak (°C/min) | | | | | | | Second DTG peak (°C/min) | | | | | | | Spiked peak | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C) | $\%W_{T_i}$[a] | $T_p$ (°C) | $\%W_{T_p}$[b] | $T_f$ (°C) | $\%W_{T_f}$[c] | $\Delta W$[d] | $T_i$ (°C) | $\%W_{T_i}$ | $T_p$ (°C) | $\%W_{T_p}$ | $T_f$ (°C) | $\%W_{T_f}$ | $\Delta W$ | $T_p$ (°C) | $\%W_{T_p}$ |
| 10.0 | 112.9 | 98.7 | 246.0 | 90.2 | 310.9 | 85.1 | 13.6 | 310.9 | 85.1 | 445.6 | 56.8 | 521.9 | 44.1 | 41.0 | | |
| 15.0 | 177.8 | 97.9 | 250.9 | 89.9 | 315.8 | 84.7 | 13.2 | 315.8 | 84.7 | 453.7 | 55.6 | 539.8 | 44.7 | 40.1 | | |
| 18.0 | 125.9 | 98.5 | 254.1 | 90.4 | 322.3 | 84.7 | 13.8 | 322.3 | 84.7 | 460.2 | 55.5 | 531.7 | 43.7 | 41.0 | | |
| 18.5 | 125.9 | 98.0 | 257.4 | 89.9 | 327.2 | 84.4 | 13.6 | 327.2 | 84.4 | 465.1 | 55.7 | | | | 528.4 | 44.7 |
| 19.0 | 127.5 | 98.5 | 259.0 | 90.3 | 325.5 | 84.7 | 13.8 | 325.5 | 84.7 | 466.7 | 55.7 | | | | 528.4 | 44.5 |
| 20.0 | 122.6 | 98.0 | 257.4 | 90.1 | 325.5 | 84.4 | 13.6 | 325.5 | 84.4 | 466.7 | 55.6 | | | | 525.2 | 45.4 |
| 25.0 | 127.5 | 98.6 | 262.2 | 90.5 | 330.4 | 84.9 | 13.7 | 330.4 | 84.9 | 474.8 | 58.0 | | | | 531.7 | 47.9 |

[a] $\%W_{T_i}$: % weight remaining at initial temperature of the peak.

[b] $\%W_{T_p}$: % weight remaining at peak temperature.

[c] $\%W_{T_f}$: % weight remaining at final peak temperature.

[d] $\Delta W = \%W_{T_i} - W_{T_f}$.

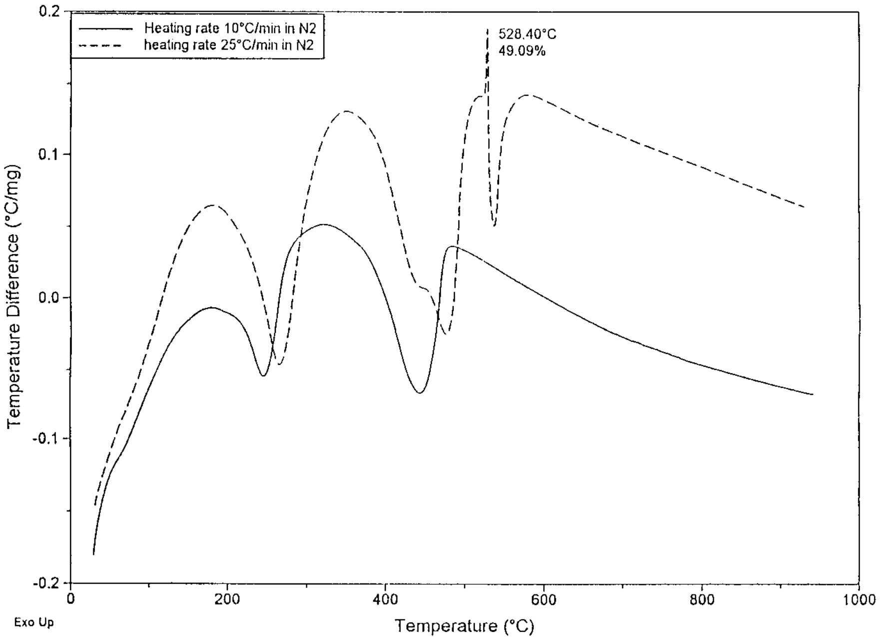

Fig. 1. Influence of heating rate on the origin of exothermic peak. DTA plot of light magnesium carbonate obtained from Fisher Scientific at a heating rate of 10°C/min and 25°C/min under an atmosphere of dry nitrogen at a flow rate of 50 ml/min.

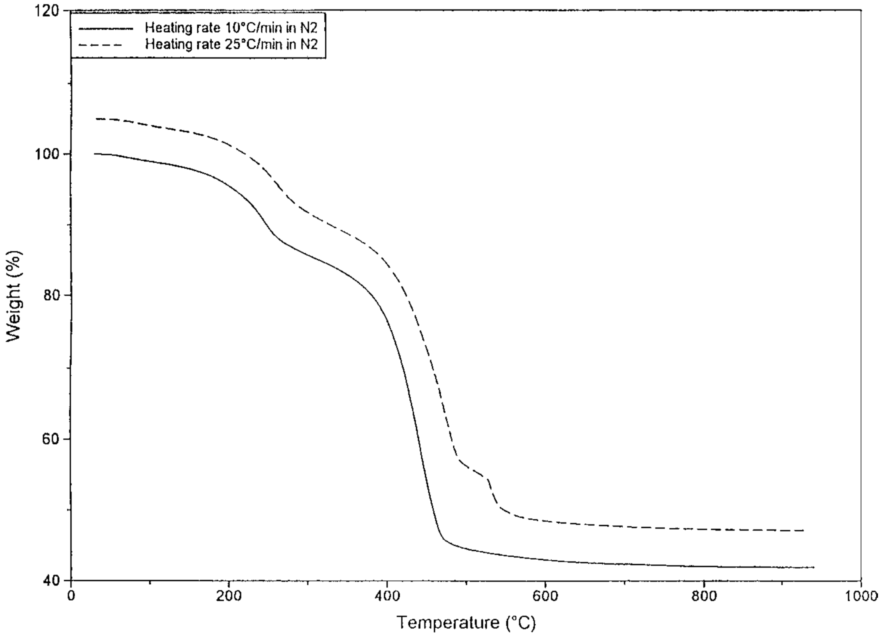

Fig. 2. Influence of heating rate on the origin of exothermic peak. TGA plot of light magnesium carbonate obtained from Fisher Scientific at a heating rate of 10 and 25°C/min under an atmosphere of dry nitrogen at a flow rate of 50 ml/min.

Table 2
DTA data for runs in nitrogen (flow rate 50 ml/min) for an initial mass of 6–8 mg for the light magnesium carbonate sample supplied by Fisher Scientific (lot # 886814)

| Heating rates (°C/min) | First endothermic peak | | | | Second endothermic peak | | | | Exothermic peak | Third endothermic peak | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C)[a] | $T_p$ (°C)[b] | $T_f$ (°C)[c] | $\Delta T$ (°C)[d] | $T_i$ (°C) | $T_p$ (°C) | $T_f$ (°C) | $\Delta T$ (°C) | $T_p$ (°C) | $T_p$ (°C) | $T_f$ (°C) |
| 10.0 | 182.3 | 244.8 | 322.6 | 140.3 | 322.6 | 443.0 | 485.7 | 163.1 | | | |
| 15.0 | 180.8 | 250.9 | 340.9 | 160.1 | 340.9 | 453.7 | 499.4 | 158.5 | | | |
| 18.0 | 177.7 | 257.0 | 345.4 | 167.7 | 345.4 | 461.3 | 504.0 | 158.6 | | | |
| 18.5 | 179.3 | 260.1 | 342.4 | 163.1 | 342.4 | 465.9 | | | 525.4 | 528.4 | 545.2 |
| 19.0 | 174.7 | 261.6 | 345.4 | 170.7 | 345.4 | 467.4 | | | 525.4 | 529.9 | 552.8 |
| 20.0 | 177.7 | 261.6 | 345.4 | 167.7 | 345.4 | 467.4 | | | 523.8 | 528.4 | 548.2 |
| 25.0 | 180.8 | 264.6 | 350.0 | 169.2 | 350.0 | 475.0 | | | 528.4 | 536.0 | 575.7 |

[a] $T_i$: initial temperature of the peak.

[b] $T_p$: peak temperature.

[c] $T_f$: final peak temperature.

[d] $\Delta T = T_f - T_i$.

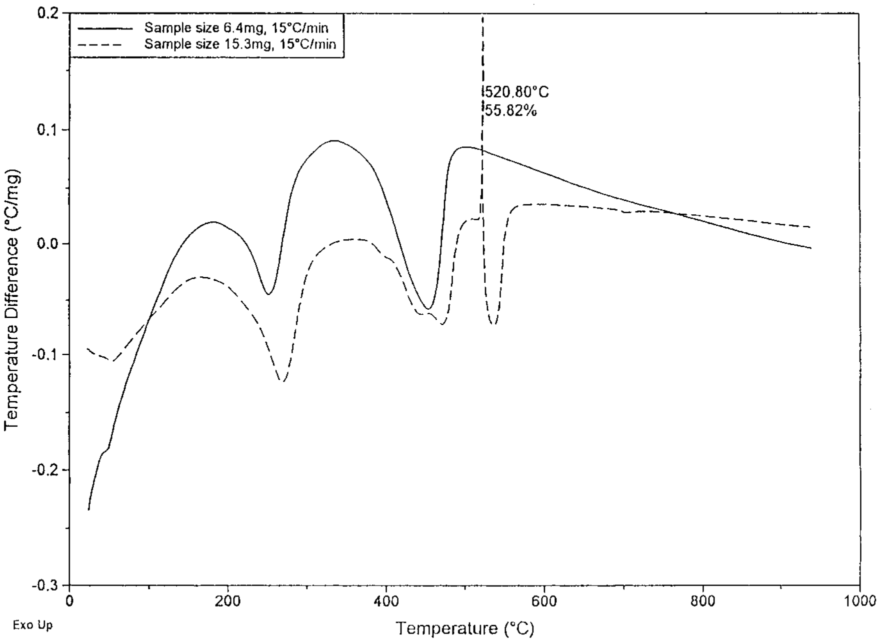

Fig. 3. Influence of sample size on the origin of exothermic peak. DTA plot of light magnesium carbonate obtained from Fisher Scientific at a heating rate of 15°C/min under an atmosphere of dry nitrogen at a flow rate of 50 ml/min and sample size of 6.4 and 15.3 mg.

### 3.3. *Effect of atmospheric conditions*

When the thermal analysis of the sample was carried out under dry nitrogen, the exothermic peak was observed at a high heating rate or when the sample size was increased. Similar results were found when the sample was analyzed in dry air. When the thermal analysis of the sample was carried out in carbon dioxide, the exothermic peak appeared, even at a slow heating rate and small sample size. Dell and Wheeler have reported the presence of an exothermic peak in carbon dioxide [3,10]. Fig. 5 shows that at 10°C/min in dry nitrogen and dry air, there was no exothermic peak on the DTA, but under the same conditions in dry carbon dioxide, the exothermic peak was present. Tables 5 and 6 and Figs. 5 and 6 summarize the effect of carbon dioxide on the magnesium carbonate sample.

According to Dell and Weller, an exothermic peak usually appears either because of delayed recrystallization or oxidation of products by the surrounding atmosphere. According to these investigators, the basic magnesium carbonate loses water to form an amorphous product and then loses carbon dioxide endothermically. In a stream of carbon dioxide, this decomposition is repressed because of the recrystallization to $MgCO_3$.

In the present study, it was found that various procedural variables also affect the origin of the exothermic peak. All these variables induce a mechanical strain on the crystal lattice of the basic hydroxy magnesium carbonate. These strains are induced by the stress of the volume change and altered solid-state lattice. When the sample size or the heating rate is increased, some of the volatile components are not allowed to escape and this eventually leads to an explosion in the material and the release of strain in the form of heat, which appears as an exotherm. An increase in the sample size induces more strain in the crystal lattice than increase in heating rate. A possible explanation can be that when the sample size is increased, the amount of carbon dioxide released by the sample also increases. This blocks the escape of carbon dioxide, which tries to release itself and causes an explosion in the sample. It has been reported earlier that decarbonation is strongly affected by the partial pressure of carbon dioxide [6]. The SEM of the solid product of decomposition produced at a

Table 3
DTA data for runs in nitrogen (flow rate 50 ml/min) for an initial mass of 15–18 mg for the light magnesium carbonate sample supplied by Fisher Scientific (lot # 886814)

| Heating rates (°C/min) | First endothermic peak | | | | Second endothermic peak | | | | Exothermic peak | Third endothermic peak | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C)[a] | $T_p$ (°C)[b] | $T_f$ (°C)[c] | $\Delta T$ (°C)[d] | $T_i$ (°C) | $T_p$ (°C) | $T_f$ (°C) | $\Delta T$ (°C) | $T_p$ (°C) | $T_p$ (°C) | $T_f$ (°C) |
| 10.0 | 157.9 | 260.1 | 343.9 | 186.0 | 343.9 | 453.7 | 514.7 | 170.8 | | | |
| 15.0 | 167.1 | 267.7 | 350.0 | 183.0 | 350.0 | 467.4 | | | 520.8 | 536.0 | 571.1 |
| 18.0 | 165.5 | 269.2 | 360.7 | 195.2 | 360.7 | 473.5 | | | 523.8 | 534.5 | 581.8 |
| 18.5 | 171.6 | 270.7 | 357.6 | 186.0 | 357.6 | 472.0 | | | 525.4 | 536.0 | 581.8 |
| 19.0 | 165.5 | 272.3 | 360.7 | 195.2 | 360.7 | 440.0 | | | 522.3 | 537.6 | 577.2 |
| 20.0 | 167.1 | 275.3 | 359.2 | 192.1 | 359.2 | 436.9 | | | 520.8 | 539.1 | 583.3 |
| 25.0 | 172.8 | 279.5 | 369.5 | 196.7 | 369.5 | 438.1 | | | 525.0 | 550.9 | 611.9 |

[a] $T_i$: initial temperature of the peak.

[b] $T_p$: peak temperature.

[c] $T_f$: final peak temperature.

[d] $\Delta T = T_f - T_i$.

Table 4

TG/DTG data for runs in dry $N_2$ (flow rate 50 ml/min) at different heating rates for the light magnesium carbonate sample supplied by Fisher Scientific (sample size 15–18 mg) (lot # 886814)

| Heating rates (°C/min) | First DTG peak (°C/min) | | | | | | Second DTG peak (°C/min) | | | | | | Spiked peak/catastrophic decrease in mass | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C) | $\%W_{T_i}$[a] | $T_p$ (°C) | $\%W_{T_p}$[b] | $T_f$ (°C) | $\%W_{T_f}$[c] | $T_i$ (°C) | $\%W_{T_i}$ | $T_p$ (°C) | $\%W_{T_p}$ | $T_f$ (°C) | $\%W_{T_f}$ | $T_p$ (°C) | $\%W_{T_p}$ | $T_f$ (°C) | $\%W_{T_f}$ | $\Delta W$[d] |
| 10.0 | 127.5 | 98.2 | 259.0 | 89.72 | 327.2 | 84.0 | 327.2 | 84.0 | 455.4 | 56.6 | 543.0 | 43.7 | | | | | |
| 15.0 | 138.9 | 97.9 | 267.1 | 89.7 | 336.4 | 85.0 | 336.4 | 85.0 | 470.0 | 63.0 | | | 521.9 | 55.8 | 583.6 | 44.6 | 11.2 |
| 18.0 | 135.6 | 98.4 | 267.1 | 90.1 | 336.9 | 84.3 | 336.9 | 84.3 | 473.2 | 58.9 | | | 526.8 | 48.9 | 593.3 | 43.6 | 5.30 |
| 18.5 | 130.8 | 98.5 | 267.1 | 90.3 | 340.1 | 84.3 | 340.1 | 84.3 | 471.6 | 61.0 | | | 525.2 | 51.6 | 604.7 | 43.9 | 7.70 |
| 19.0 | 140.5 | 97.8 | 268.7 | 89.7 | 336.9 | 83.9 | 336.9 | 83.9 | 463.5 | 64.8 | | | 523.5 | 56.9 | 609.6 | 43.1 | 13.8 |
| 20.0 | 138.9 | 97.7 | 270.3 | 89.5 | 336.9 | 83.7 | 336.9 | 83.7 | 437.5 | 71.9 | | | 520.3 | 60.8 | 590.1 | 42.9 | 17.9 |
| 25.0 | 129.1 | 98.5 | 273.6 | 90.2 | 349.9 | 83.9 | 349.9 | 83.9 | 434.3 | 74.7 | | | 523.5 | 65.5 | 598.2 | 42.8 | 22.7 |

[a] $\%W_{T_i}$: % weight remaining at initial temperature of the peak.

[b] $\%W_{T_p}$: % weight remaining at peak temperature.

[c] $\%W_{T_f}$: % weight remaining at final peak temperature.

[d] $\Delta W = \%W_{T_i} - W_{T_f}$.

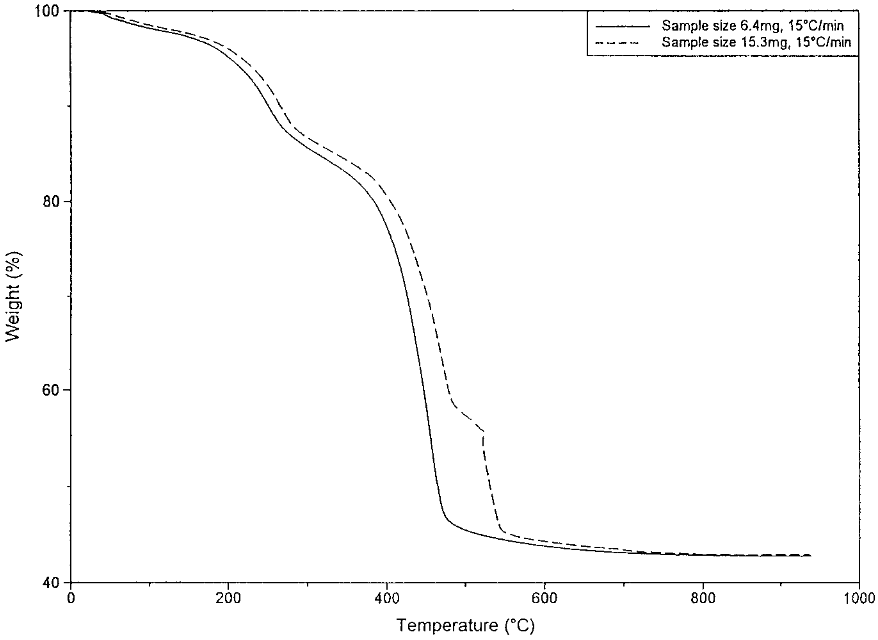

Fig. 4. Influence of sample size on the origin of exothermic peak. TGA plot of light magnesium carbonate obtained from Fisher Scientific at a heating rate of 15°C/min under an atmosphere of dry nitrogen at a flow rate of 50 ml/min and sample size of 6.4 and 15.3 mg.

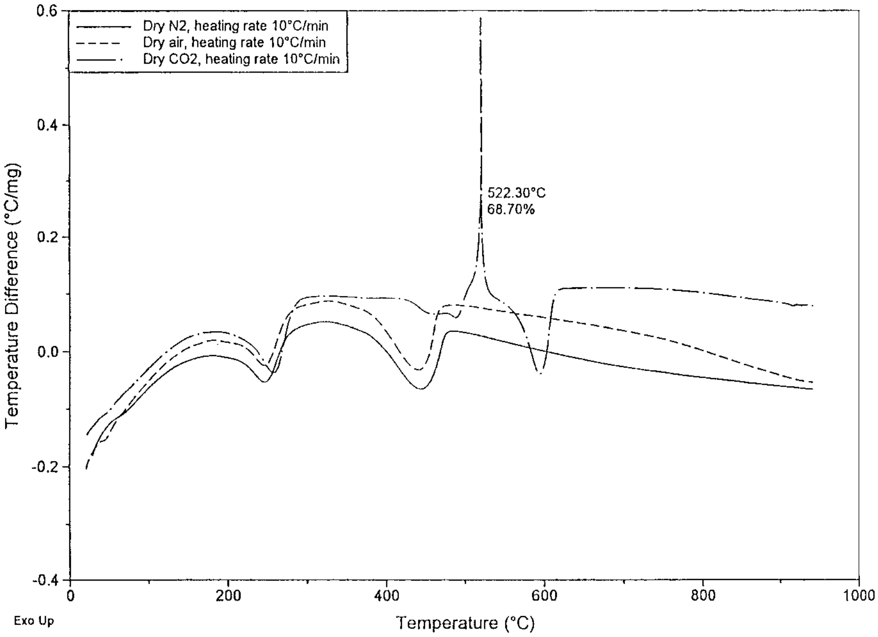

Fig. 5. Influence of atmospheric conditions on the origin of exothermic peak. DTA plot of light magnesium carbonate obtained from Fisher Scientific at a heating rate of 10°C/min under an atmosphere of dry nitrogen, dry air and dry carbon dioxide at a flow rate of 50 ml/min.

Table 5

TG/DTG data for runs in dry $CO_2$ (flow rate 50 ml/min) at different heating rate for the light magnesium carbonate sample supplied by Fisher Scientific (sample size 7–10 mg) (lot # 886814)

| Heating rates (°C/min) | First DTG peak (°C/min) | | | Second DTG peak (°C/min) | | | | | | Spiked peak | | | Fourth DTG peak (°C/min) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C) | $\%W_{T_i}$[a] | $T_p$ (°C) | $\%W_{T_p}$[b] | $T_f$ (°C) | $\%W_{T_f}$[c] | $T_i$ (°C) | $\%W_{T_i}$ | $T_p$ (°C) | $\%W_{T_p}$ | $T_p$ (°C) | $\%W_{T_p}$ | $T_p$ (°C) | $\%W_{T_p}$ | $T_f$ (°C) | $\%W_{T_f}$ |
| 10.0 | 132.4 | 97.8 | 257.4 | 88.6 | 309.3 | 85.1 | 422.9 | 80.6 | 487.8 | 74.3 | 518.7 | 71.6 | 591.7 | 50.4 | 638.7 | 41.5 |
| 15.0 | 143.7 | 97.7 | 262.2 | 89.7 | 315.8 | 85.9 | 426.2 | 81.5 | 487.8 | 75.8 | 520.3 | 73.3 | 596.6 | 52.6 | 697.2 | 43.8 |
| 18.0 | 127.5 | 98.0 | 273.6 | 89.0 | 341.8 | 84.6 | 411.5 | 81.5 | 484.6 | 75.4 | 517.0 | 72.9 | 599.8 | 49.4 | 674.5 | 41.8 |
| 19.0 | 135.6 | 98.0 | 267.1 | 89.6 | 319.0 | 85.9 | 411.5 | 82.1 | 486.2 | 76.1 | 518.7 | 73.5 | 598.2 | 52.0 | 674.5 | 43.9 |
| 25.0 | 135.6 | 97.9 | 268.7 | 89.8 | 343.4 | 85.5 | 424.5 | 81.9 | 489.5 | 76.5 | 518.7 | 74.4 | 603.1 | 53.1 | 692.3 | 45.0 |

[a] $\%W_{T_i}$: % weight remaining at initial temperature of the peak.

[b] $\%W_{T_p}$: % weight remaining at peak temperature.

[c] $\%W_{T_f}$: % weight remaining at final peak temperature.

Table 6
DTA data for runs in $CO_2$ (flow rate 50 ml/min) for an initial mass of 7–10 mg for the light magnesium carbonate sample supplied by Fisher Scientific (lot # 886814)

| Heating rates (°C/min) | First endothermic peak | | | | Second endothermic peak | | Exothermic peak | Third endothermic peak | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C)[a] | $T_p$ (°C)[b] | $T_f$ (°C)[c] | $\Delta T$ (°C)[d] | $T_i$ (°C) | $T_p$ (°C) | $T_p$ (°C) | $T_p$ (°C) | $T_f$ (°C) |
| 10.0 | 171.7 | 257.0 | 310.9 | 139.2 | 418.6 | 475.0 | 520.7 | 594.0 | 641.2 |
| 15.0 | 177.7 | 266.2 | 316.5 | 138.8 | 417.1 | 464.36 | 520.77 | 600.1 | 642.8 |
| 18.0 | 177.7 | 275.3 | 334.8 | 157.1 | 426.2 | 473.5 | 517.7 | 601.6 | 644.3 |
| 19.0 | 180.8 | 269.2 | 333.24 | 152.4 | 426.24 | 475.0 | 517.7 | 601.6 | 639.7 |
| 25.0 | 186.9 | 272.3 | 336.3 | 149.4 | 412.6 | 479.7 | 522.3 | 607.7 | 651.9 |

[a] $T_i$: initial temperature of the peak.
[b] $T_p$: peak temperature.
[c] $T_f$: final peak temperature.
[d] $\Delta T = T_f - T_i$.

temperature just before the exotherm in an atmosphere of carbon dioxide shows scattered particles. In the process of the experiment, it was observed that when the sample size is small, the MgO produced at the end of the reaction (as it tends to be denser than magnesium carbonate), forms a compact dense mass in the crucible. When the sample size is increased, the MgO produced at the end is not compact but is fluffy and dispersed. This explanation would support the above result.

## 4. Summary

It can be summarized that the heating rate, sample size and atmospheric conditions influence the exothermic peak.

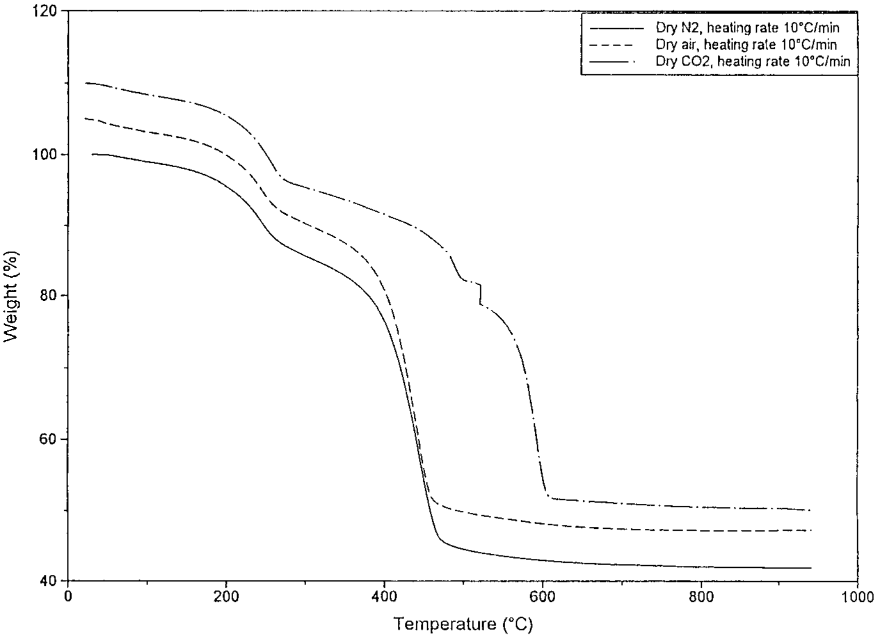

Fig. 6. Influence of atmospheric conditions on the origin of exothermic peak. TGA plot of light magnesium carbonate obtained from Fisher Scientific at a heating rate of 10°C/min under an atmosphere of dry nitrogen, dry air and dry carbon dioxide at a flow rate of 50 ml/min.

1. An exothermic peak is observed in an atmosphere of nitrogen and air if the heating rate is increased.
2. An exothermic peak is observed at a lower heating rate if the size of the sample is increased. Increase in the sample size increases the area of the exothermic peak.
3. An exothermic peak appears at a lower heating rate and decrease sample size if the atmosphere is changed to carbon dioxide.
4. The exotherm is always accompanied by a sharp increase in rate of weight loss, which would be consistent with mechanical stress resulting in breakdown of the sample into smaller fragments with an increase in the reaction interface.

## 5. Conclusion

If a constraint is imposed on the system, then the stress imposed in the system is only relieved by the mechanical breakdown of the crystallites and a release of the excess energy in the form of heat.

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