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Calorimetry a method to be used to characterise pyrolytically decarboxylated bicarbonate and assess its stability at elevated humidities

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Abstract

Microcalorimetry was used to characterise bicarbonate after treatment at high temperatures. By measuring the heat flow from a sample of bicarbonate at 100% relative humidity, the net exothermic contribution could be used to estimate the fraction of pyrolytically formed Na_2CO_3. The enthalpy value corresponding to the heat of solution of Na_2CO_3 was also applicable to a physical mixture of $NaHCO_3/Na_2CO_3$. However, from the characteristic peaks of the heat flow versus time curve, pyrolytically formed Na_2CO_3 could be distinguished from that present in the physical mixture. The different bicarbonate batches of varying degree of pyrolytic decarboxylation were also observed at an elevated relative humidity of 54%. From these measurements it could be inferred that a decarboxylation of up to 4.5% could be allowed without any significant effect on the stability of bicarbonate at 54%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetry; Sodium bicarbonate; Sodium carbonate; Relative humidity; Enthalpy; Pyrolytic decarboxylation

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1. Introduction

Sodium bicarbonate, $NaHCO_3$, the mildest of all sodium alkalis, is widely used not only in pharmaceuticals, but also in food, rubber, plastics, fire extinguishing agents, household cleaning products, etc. As a component of pharmaceutical formulations, $NaHCO_3$ is used as a carbon dioxide source in effervescent products or as a compound to create alkaline pH in preparations. Therapeutically, $NaHCO_3$ may be used in the treatment of metabolic acidosis and as a major component in dialysis fluids (Delin et al., 1988; Gable and Weller, 1994).

$NaHCO_3$ is known to decompose into sodium carbonate, Na_2CO_3, carbon dioxide and water depending on relative humidity, pressure and temperature (Usui and Carstensen, 1985; Gable and Weller, 1994; Kuu et al., 1998). Thermal decomposition of $NaHCO_3$ has been studied under various conditions (different pressures, open and closed systems, various atmospheres) using differ-

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ential thermal analysis (Barrall and Rogers, 1996), thermal gravimetric analysis (Akosman and Walters, 1994) and X-ray diffraction (XRD) (Shefter et al., 1974–1975). These investigations provide evidence for the pyrolytic decarboxylation of $NaHCO_3$ into Na_2CO_3.

Effervescent products are in comparison to most other pharmaceutical formulations more susceptible to humidity. The stability of effervescent products increases by introducing Na_2CO_3 which acts as a moisture scavenger (White, 1963; Usui and Carstensen, 1985). Sodium carbonate can be introduced either by physically mixing it with the components or by using heat, thereby, partly converting $NaHCO_3$ into Na_2CO_3.

Isothermal microcalorimetry is a non-invasive and non-destructive technique. The high sensitivity of the calorimeter associated with the possibility of continuously monitoring the ongoing reaction processes, makes the technique highly powerful in the study of complex heterogeneous reaction systems, often without the need for any further analytical investigation (Ahmed et al., 1996; Angberg, 1992; Willson et al., 1995, 1996).

The aim of the study presented here, was to study the interactions of partly decarboxylated bicarbonate with water vapour using isothermal microcalorimetry. Two relative humidities (RH) were used — 100% RH for the detection and quantitative estimation of the degree of decarboxylation, and 54% RH for assessing the effect of decarboxylation on the stability of bicarbonate at an elevated RH.

2. Materials and methods

2.1. Materials

$NaHCO_3$ was taken from Codex Fein, Solvay, France and Na_2CO_3, p.a. from Merck, Germany. The water used was of reagent grade obtained by Milli-Q filtration.

2.2. Preparation and characterisation of sample

Five portions of $NaHCO_3$ were incubated at 90°C in a hot air oven at 15% RH for five different time periods ranging from 35 to 150 min. The degree of pyrolytic decomposition was determined by the amount of Na_2CO_3 generated using direct pH measurements. The pH was measured in a 1% (w/w) solution at 25°C, 3 min after dissolution of samples and standard mixtures of $NaHCO_3/Na_2CO_3$.

A scanning electron microscope (JSM-5310, Jeol, Japan) was used to study the morphological surface changes related to the heat treatment of $NaHCO_3$ on gold sputtered samples.

2.3. Calorimetry

A four-channel heat conduction microcalorimeter (TAM 2277, Thermometric AB, Järfälla, Sweden) was used (Suukkuusk and Wadsö, 1982). The calorimeter was calibrated electrically and the measurements were conducted at 37°C in sealed 1.3-ml stainless steel vessels. Constant RH inside the measuring vessel was achieved by inserting a small test tube filled with either distilled water for 100% RH or saturated NaBr solution for 54% RH (Nyqvist, 1983; Angberg, 1992). Calorimetric analyses were performed on samples consisting of pure $NaHCO_3$, pyrolytically decarboxylated $NaHCO_3$ and a physical mixture of $Na_2CO_3/NaHCO_3$ (7.8% w/w). The samples weighed between 0.10 and 0.30 g. The heat flow was monitored for 2–6 h and the observed thermal power P (μW) was recorded and integrated. The weight and pH of the sample were determined at the end of each experiment.

2.4. Statistic

Numerical data are expressed as mean ± S.D. Correlation coefficients were obtained by linear regression analysis.

3. Results and discussion

Pyrolytic decarboxylation of $NaHCO_3$ caused morphological changes that could be directly correlated to the time of incubation at elevated temperature. Fig. 1 is a photograph of the altered surface of a bicarbonate sample upon heat treatment. Already after 35 min at 90°C, 1.9% of the bicarbonate had been converted to Na_2CO_3, which could be identified as number of small crystals formed on the surface of the $NaHCO_3$ crystals. The fractions of decarboxylation determined by the means of pH measurements of the amount of formed Na_2CO_3 of the heat-treated samples were 1.9, 4.1, 6.5, 7.8 and 8.8% (w/w).

The thermal power curves obtained from calorimetric runs of different samples at 100% RH are shown in Fig. 2. All the calorimetric traces obtained from several measurements are reproducible. The samples studied were pure bicarbonate, partly decarboxylated bicarbonate and $NaHCO_3/Na_2CO_3$ in a physical mixture. The curve for pure $NaHCO_3$ consists of an initial sharp exothermic phase that can probably be attributed to the adsorption of water. Approximately 10 min later the signal changes to the endothermic side and returns exponentially to the baseline. For pure bicarbonate at 100% RH, the sum of the endothermic and exothermic contributions is zero owing to a compensation of the two interactions. At 54% RH, a small endothermic effect of 0.46 J/g was recorded. The endothermic signal recorded at both the humidities is probably due to decarboxylation of $NaHCO_3$ which is in agreement with the data presented by Kuu et al.

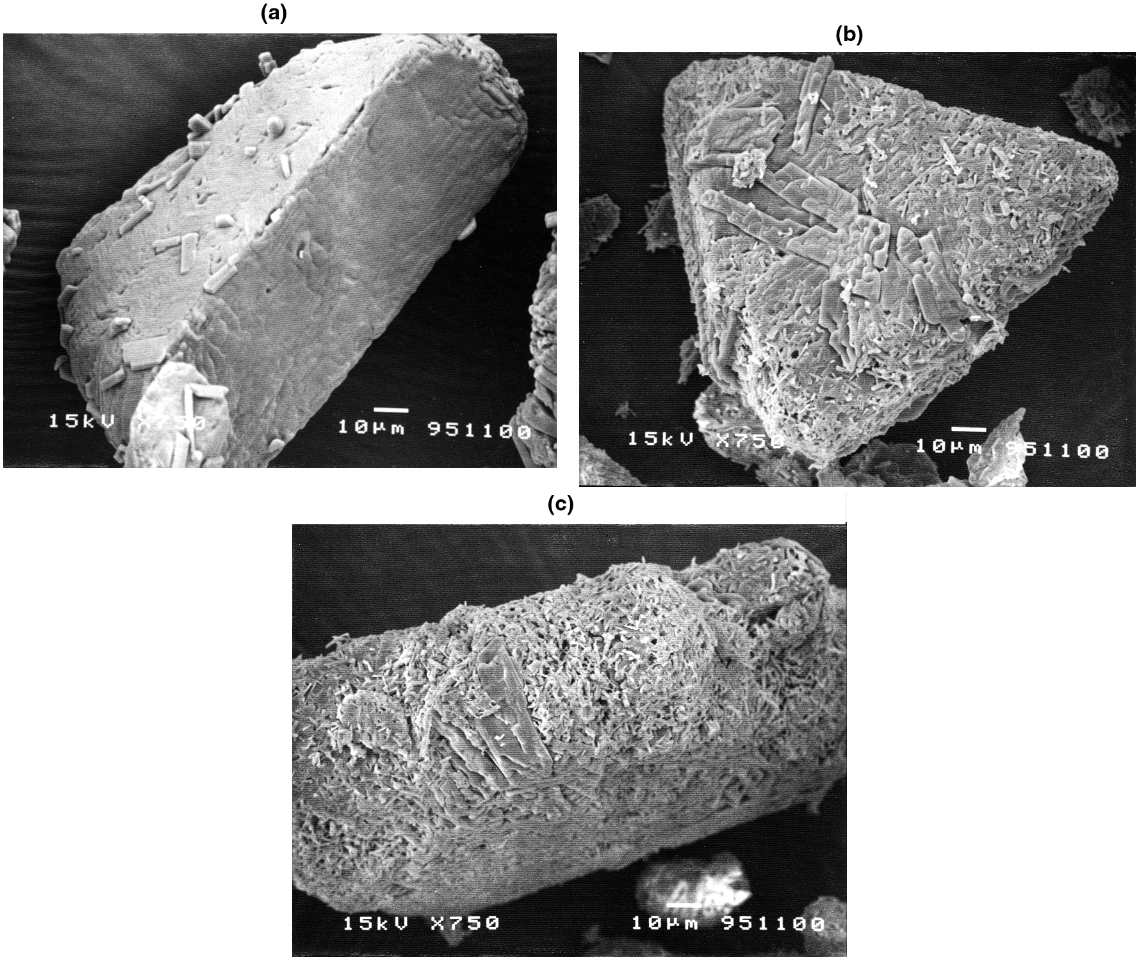

Fig. 1. Scanning electron micrographs of $NaHCO_3$: (a) untreated; (b) after thermal decomposition representing decarboxylation of 1.9% and (c) after heat treatment with a decarboxylation of 4.4%.

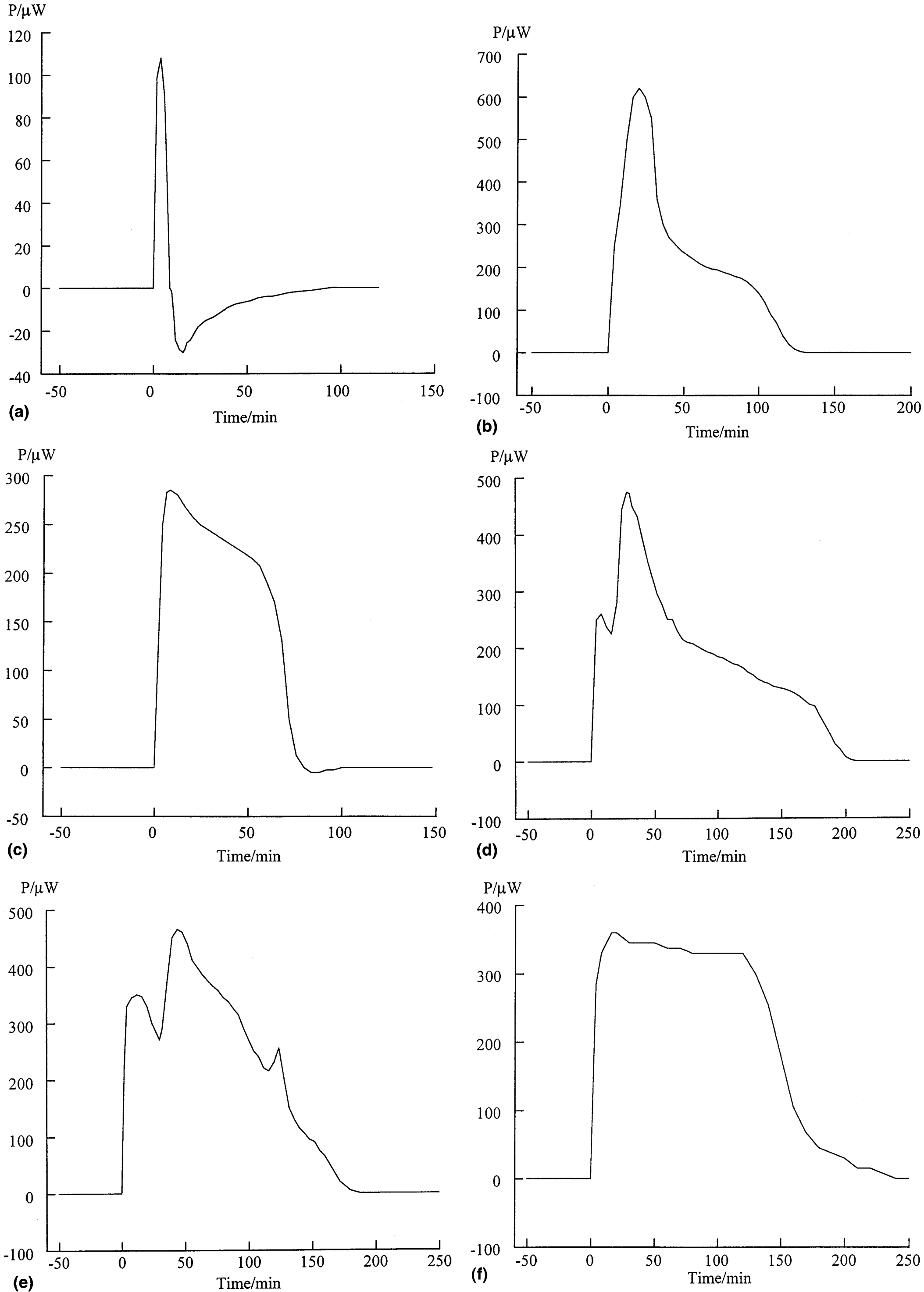

Fig. 2. Illustrations of thermal power profiles obtained at 100% RH for (a) pure NaHCO$_3$; and (b) pyrolytically decarboxylated samples of 1.9; (c) 4.1; (d) 6.5; (e) 7.8; and (f) a physical mixture of 7.8% of Na$_2$CO$_3$.

Table 1
Enthalpies of interaction between pyrolytically decarboxylated $NaHCO_3$ and water vapour at 37°C in kJ/mol of $NaHCO_3$ and Na_2CO_3, respectively[a]

Fraction Na_2CO_3 (w/w)	ΔH (kJ/mol) $NaHCO_3$ (54% RH)	ΔH (kJ/mol) $NaHCO_3$ (100% RH)	ΔH (kJ/mol) Na_2CO_3 (54% RH)	ΔH (kJ/mol) Na_2CO_3 (100% RH)
0	0.04 ± 0.001	0		
1.9	0.03 ± 0.007	-0.44 ± 0.03	2.12 ± 0.53	-28.5 ± 0.53
4.1	0.02 ± 0.01	-0.92 ± 0.04	0.52 ± 0.26	-27.2 ± 0.26
6.5	-0.24 ± 0.02	-1.48 ± 0.13	-4.20 ± 0.32	-26.9 ± 0.32
7.8	-0.40 ± 0.01	-1.98 ± 0.01	-6.02 ± 0.14	-29.5 ± 0.14
8.8	-0.41 ± 0.01	-2.05 ± 0.12	-5.30 ± 0.12	-26.9 ± 0.12

[a] Mean values $n = 9 \pm$ S.D.

(1998). As illustrated in Fig. 2, the calorimetric traces obtained at 100% RH for pyrolytically decarboxylated samples exhibit different patterns depending on the degree of decarboxylation. For samples that have been decarboxylated up to 4%, a pronounced exothermic peak can be observed at the first part of the curve. At 6.5% decarboxylation, the result from the samples is characterised by the appearance of two major peaks, and if the decarboxylation exceeded 7.8%, three well-defined peaks appeared. In contrast, no distinct peaks could be seen in the calorimetric graph for a physical mixture with a fraction of 7.8% Na_2CO_3 at 100% RH as shown in Fig. 2. At 54% RH, no abnormalities of the calorimetric traces for the pyrolytically decarboxylated samples were observed. The thermal power reach maximum endothermic/exothermic values after about 40–60 min, thereafter, declining to baseline within the stipulated time period. The vapour induced peaks on the thermal power curves for pyrolytic decarboxylated sample indicate a plausible formation of different intermediates during heating (Vanderzee, 1982). The difference between the physical mixture and the thermally converted sample containing the same amount of Na_2CO_3 could possibly be explained by differences in contact area, crystallinity of Na_2CO_3, etc. Such differences in reactivity related to surface energy effects have been described by Waterfield et al. (1968) for microcrystalline Na_2CO_3 and Na_2CO_3 prepared by thermal decomposition of sodium bicarbonate.

It has been shown that at certain atmosphere conditions and temperatures $NaHCO_3$ can decompose forming trona or Wegcheider's salt (Mitkevich, 1958; Vanderzee, 1982; Vanderzee and Wigg, 1981; Barrall and Rogers, 1996). However, according to Shefter et al. (1974–1975) a non-crystalline intermediate of anhydrous Na_2CO_3 was formed on the surface of the $NaHCO_3$ crystal in an open system between 82 and 95°C and there was no indication of any formation of crystalline hydrates or complex salts. In the present study, the samples were prepared at 90°C in an open system at low humidity and the formation of Na_2CO_3 on the surface was to be expected. The thermodynamic data on Na_2CO_3 (Berg and Vanderzee, 1978) indicates that a large exothermic effect is to be expected when carbonate reacts with liquid water. If the interaction starts with a surface reaction between Na_2CO_3 crystals and water vapour the thermal power should increase parallel to the decarboxylation which is in full agreement with the calorimetric results (Table 1).

Whereas the total heat for pure bicarbonate at 100% RH was 0, a fraction of Na_2CO_3 formed by pyrolytic decarboxylation of bicarbonate gave an exothermic contribution. If the heat derived from measurements of samples at 100% RH were correlated to the degree of decarboxylation, a slope of -27.8 ± 1.2 kJ/mol Na_2CO_3 ($r = 0.996$) was obtained (Fig. 3). It was thus, possible to estimate the fraction of pyrolytically formed Na_2CO_3 from the exothermic contribution reflecting the heat of the solution of Na_2CO_3. The heat of the solution of Na_2CO_3 at 25°C is -26.7 kJ/mol (Berg and Vanderzee, 1978) and it is known to increase with temperature (Mischenko and Poltoratskiy, 1976). The ΔH value obtained from the 7.8% physical mixture was almost the same as that for the corresponding pyrolytically decarboxylated sample, the difference being that the specific peaks were present for the physical mixture.

No change in pH measured before or after calorimetry was observed for the samples indicating that the ratio $Na_2CO_3/NaHCO_3$ was unaffected by the calorimetric procedure.

The change in weight recorded after calorimetry at 54% RH was less than 0.2% if the decarboxylation did not exceed 7.8%. However, at a decarboxylation of 8.8% the change in weight was 0.6%. At 100% RH the weight increase was significantly higher (5–7%) and could be correlated to the degree of carboxylation. It can be concluded that the increase in weight at 100% RH was solely due to the uptake of water, as other reactions are not likely to occur as judged from the static pH during the course of the experiment.

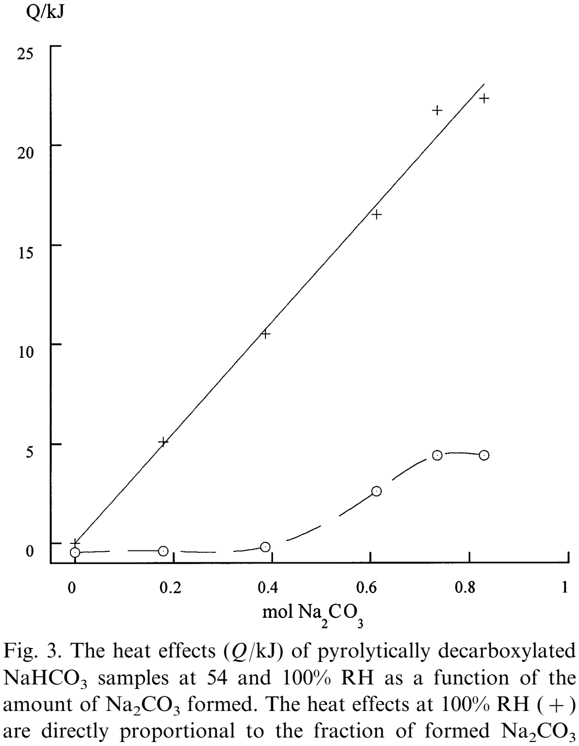

Fig. 3. The heat effects (Q/kJ) of pyrolytically decarboxylated $NaHCO_3$ samples at 54 and 100% RH as a function of the amount of Na_2CO_3 formed. The heat effects at 100% RH (+) are directly proportional to the fraction of formed Na_2CO_3 whereas the values at 54% RH (○) shows how the heat treatment affects the stability at this elevated humidity.

4. Conclusions

Calorimetry proved to be a very sensitive method to characterise the decarboxylation of $NaHCO_3$ and determine the stability at high RH. The studies indicated that the degree of pyrolytic decarboxylation should not exceed 4.5% in order to avoid detrimental effects on the stability of bicarbonate at 54% RH. A high humidity of 100% probably causes a complete dissolution of Na_2CO_3 formed on the surface of a sample of $NaHCO_3$; the process not having any other effects upon $NaHCO_3$ itself. Pyrolytically formed Na_2CO_3 could be distinguished from Na_2CO_3 in a physical mixture by the presence of specific hydration peaks. The investigation presented here shows that microcalorimetry can be used to produce a large set of data from the complex. However, further investigations are required to fully understand the mechanism of interactions between water vapour and pyrolytically decarboxylated $NaHCO_3$.

Acknowledgements

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