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# THE THERMAL DECOMPOSITION OF $NaHCO_3$
## Renewed studies by DSC, SEM and FT-IR

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## Abstract

New EGA findings revealed that the small endothermal event preceding that of the main decomposition of commercial $NaHCO_3$ involves the simultaneous evolution of water and $CO_2$. At very high sensitivity, EGA experiments evidenced that the above (limited) evolution of gases also took place from the recrystallized material for which thermal methods gave no indication of endotherms.

Careful reexamination of previous DSC results indicated that for one kind of recrystallized material a very small endotherm had been neglected. Renewed experiments revealed that this endotherm can be enhanced if the samples are prepared by crushing and sieving in a wet atmosphere. Parallel FT-IR experiments on commercial and recrystallized materials demonstrated the presence of carbonate in samples that had previously been taken just beyond the first small endotherm; this confirmed the EGA results. SEM experiments showed that surface texture changes take place when samples are heated to temperatures just above that of the preliminary endotherm. On the basis of these new findings, the interpretation previously given to the small endotherm is revised and detailed knowledge is gained on the mechanism of decomposition of $NaHCO_3$.

**Keywords:** DSC, FT-IR, kinetics and mechanism, SEM, sodium hydrogencarbonate, thermal decomposition

## Introduction

A previous report on the decomposition of $NaHCO_3$ (either commercial powders or differently stored recrystallized material [1]) gave quantitative evidence of the presence of a small endotherm, at ca. 85°C, preceding the one corresponding to the main decomposition of commercial products. Accurate EGA experiments [2] revealed that, during this small endotherm, the simultaneous evolution of water and $CO_2$ occurred. This contrasted with the previous interpretation

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(based on the Pascal report [3] and the lack of the low-temperature endotherm in the thermal curves of decomposing recrystallized materials), which attributed the endotherm to the dehydration of hydrated carbonate formed on the surfaces of commercial crystals during long storage in wet atmospheres. Therefore, a reinterpretation of the first endotherm was necessary, which might entail a revision of the mechanism proposed for the main decomposition.

To gain a detailed insight, we decided to reexamine the thermal findings of the previous work and to perform the new DSC, FT-IR and SEM experiments described below.

## Experimental

The sodium hydrogencarbonate used in the present experiments was either of commercial origin (Solvay) or was the recrystallized material named DXt in the previous report [1]. Mass loss determinations (see Table 1 in Ref. [1]) indicate that the purity of the Solvay product is comparable to that of the other commercial preparations, while the purity of DXt is higher than that of the parent 99.5% Merck p.a. product, whose analytical data are to be found in the Merck catalogue.

For the renewed DSC studies, the samples were prepared in a dry box by crushing DXt crystals with a mortar and pestle in an atmosphere of known relative humidity (RH), sieving and transferring part of the 125–106 μm fraction into previously weighed aluminium crucibles; these were then loosely covered with weighed aluminium lids. The sample pans thus prepared were removed from the dry box, rapidly weighed and transferred into the cell of a Perkin-Elmer DSC7, the latter operations taking less than 2 min. The thermal experiments were immediately started at a scan rate of 5 K $\text{min}^{-1}$ and a flushing dry nitrogen flow of 16 ml $\text{min}^{-1}$. In some instances, the DSC runs were interrupted just after the initial small endotherm, to collect FT-IR spectra of the residue and to check for mass loss. Inside the dry box, three values of RH (measured by calibrated hair hygrometers) were produced: a) 35%, ensured by the presence of $CaCl_2 \cdot 6H_2O$ powder; b) 80%, in the presence of a saturated aqueous solution of $KNO_3$; c) 90%, in the presence of a saturated aqueous solution of $K_2SO_4$. During the preparation of the samples, the temperature inside the dry box was 20±2°C.

FT-IR spectra of i) $Na_2CO_3$, Merck p.a., ii) $Na_2CO_3 \cdot 10H_2O$, Merck p.a., iii) DXt, iv) $NaHCO_3$, Solvay, v) samples taken from the above wet preparations, and vi) samples of the above bicarbonates taken by DSC just above the 85°C endotherm were recorded, after pelletization with KBr, using an FTS-40 Bio-Rad FT-IR spectrometer.

The surfaces of the Solvay and DXt materials, either as such or after having been taken to 105°C by DSC, were examined, after graphitization with a Jeol JEE 4B apparatus, using a Philips 515 scanning electron microscope to ascertain whether texture changes had taken place during the low-temperature endotherm.

## Results

The EGA finding concerning the simultaneous evolution of water and $CO_2$ at 85°C, in correspondence with the low-temperature endotherm of commercial samples, was also found to hold [2] for our DXt preparation, for which no indication of a preliminary endotherm had been found by thermal methods. Hence, a careful reexamination of all the DSC curves previously recorded for both DXt and WXt samples was undertaken. (We recall here that the WXt material originated from the same crystallization batches of DXt, but was stored, in air, in a test-tube closed with a plastic stopper [1].) This revealed that, when the 70–110°C range of the recorded thermal curves was expanded to the maximum sensitivity, very small endotherms (ca. 0.05 J $g^{-1}$) were detectable in the range 80–95°C for almost all the WXt samples (Fig. 1), but were absent for the DXt samples, thereby indicating that the sensitivity of the thermal apparatus was insufficient in this case.

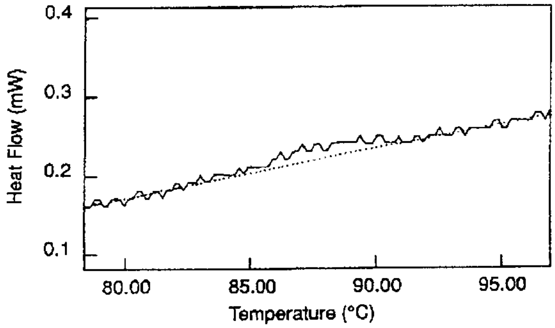

**Fig. 1** The small endotherm present in the thermal curves of the WXt samples of the previous work

Three complete decomposition curves of samples of DXt prepared at the different *RH* values described above are presented in Fig. 2. They evidence that crushing in high *RH* enhances the low-temperature endotherm well beyond the limit of sensitivity of the thermal apparatus. In particular, while no peak is found at 35% *RH* in agreement with previous results, the enthalpic change is *ca.* 0.6 J $g^{-1}$ at 80% *RH* and ca. 4.2 J $g^{-1}$ at 90% *RH*. It is also evident that the small endotherms are shifted towards higher temperatures on increase of the *RH*. The measured shifts in the whole curves correspond to those already observed [1]. The mass losses after complete thermal decomposition are independent of *RH* and always correspond to those reported previously for DXt and WXt [1]. For samples prepared at 90% *RH*, where heating was interrupted just beyond the 85°C endotherm for FT-IR purposes, a small mass loss of the order of 0.7% of the stoichiometric amount could be confirmed, but this determination is affected by large errors. The enthalpic changes for the complete decomposition of the samples prepared at 35% *RH* match the value previously reported for DXt, while those corresponding to samples prepared at higher *RH* agree better with the value reported for WXt [1].

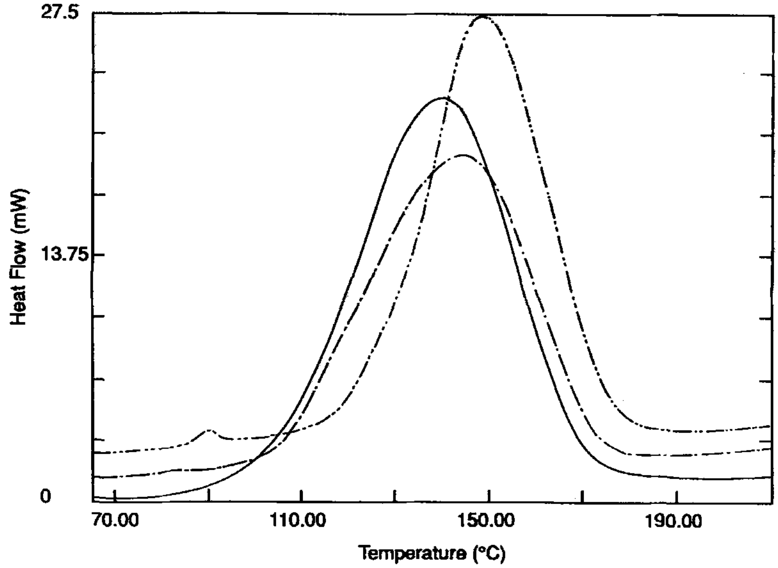

**Fig. 2** Thermal curves of samples of crushed DXt prepared at 35% *RH* (—), 80% *RH* (– –) and 90% *RH* (–··–). For illustrative purposes, the curves have been shifted along the ordinate

The kinetic analysis of the thermal curves (see [1] for details) confirms the overall 'order of reaction type' obedience with $n$=1. The kinetic parameters deduced from the 35% *RH* curves correspond almost exactly to the values previously reported for DXt [1]. In contrast, the values calculated for ln$A$ and $E_a$ from the thermal curves of the 80 and 90% *RH* samples are significantly lower than those previously reported for WXt [1]. In particular, the values deduced from the Perkin-Elmer software are $E_a$=92.5±5.6 kJ mol$^{-1}$, ln($A$/s$^{-1}$)=21.4±1.6 and $n$= 0.97±0.06. The corresponding values evaluated from the differential method ($n$=1) are $E_a$=98.2±1.1 kJ mol$^{-1}$ and ln($A$/s$^{-1}$)=21.2±0.8. These discrepancies relative to the previous findings are justified below.

In Fig. 3a, the 800–900 cm$^{-1}$ ranges of the FT-IR spectra of crushed DXt (□), DXt crushed in 90% *RH* (•) and a Solvay sample (○) are superimposed, showing the band peaking at 835 cm$^{-1}$ typical of $NaHCO_3$, attributed to the bending out-of-plane of $HCO_3^-$ [4]. In the spectrum of the Solvay sample, a shoulder at 849 cm$^{-1}$ is also present. In Fig. 3b, referring to the same range of wavenumbers, the FT-IR spectra of the Solvay sample and of DXt crushed in 90% *RH*, both brought by DSC to 105°C are reported; they show a distinct peak at 880 cm$^{-1}$,

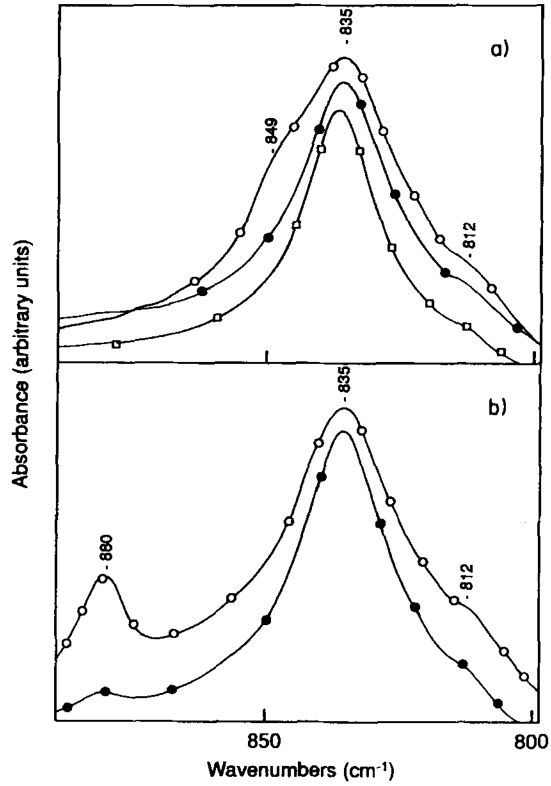

**Fig. 3** The 800–900 $cm^{-1}$ region of the FT-IR spectra a) of DXt crystals crushed at 35% *RH* (□) or 90% *RH* (•) and of a sample of crystals of the Solvay commercial product (o); b) of samples of the two latter compounds taken by DSC to 105°C

typical of $Na_2CO_3$ and attributed to an internal mode of $CO_3^{-2}$ [4]. This peak is clearly visible in the spectrum (not reported) of $Na_2CO_3$ Merck p.a. Another significant difference is found when the FT-IR spectra of the same materials as in Fig. 3a, but in the range 3200–3500 $cm^{-1}$, are compared (Fig. 4). The DXt sample does not display any particular spectral feature, while for the other two materials a broad band centred at about 3470 $cm^{-1}$ is observed, due to the –OH stretching of either adsorbed water or of crystal hydrate water. In the spectrum of $Na_2CO_3 \cdot 10H_2O$ Merck p.a., the broad band due to the –OH stretching of the crystal hydrate water is centred at about 3200 $cm^{-1}$.

SEM micrographs of Solvay crystal surfaces before and after heating to 105°C are shown in Fig. 5; the corresponding micrographs for DXt crystals are given in Fig. 6. Observation of the low and medium-magnification micrographs in Fig. 5 reveals a significant increase in the amount of recrystallized material present on the surface of the sample taken to 105°C; high-magnification mi-

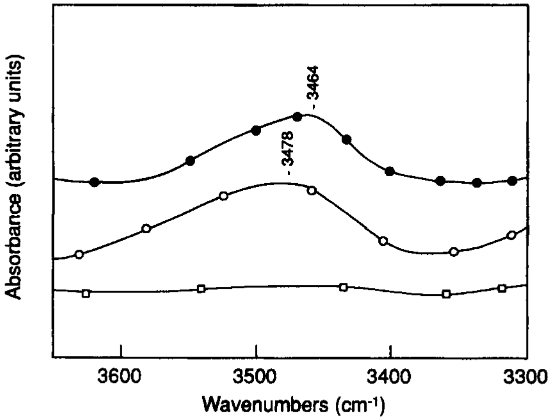

**Fig. 4** The 3300–3700 $cm^{-1}$ region of the FT-IR spectra of the same materials as in Fig. 3a (symbols as in Fig. 3a)

crographs demonstrate that a marked change has taken place in the surface texture, with the formation (or development) of several pit-like features. In comparison with that of the Solvay crystals, the surface of the DXt material (Fig. 6) is smooth and almost free of recrystallized material, whose increase on thermal treatment is not so apparent as in the previous case; pit formation and surface corrugation are less evident; on the whole, the behaviour of the DXt material parallels that of the Solvay crystals, even if the observed phenomena are notably less pronounced.

## Discussion

The new findings and the reexamination of the previous thermal results shed new light on the mechanism of decomposition of $NaHCO_3$ crystals. The EGA results [2] were of paramount importance from two respects: i) they provide evidence of the simultaneous evolution of water and $CO_2$ at *ca.* 85°C, and ii) they show that such evolution also takes place for the dry DXt material, for which no evidence of the small endothermal event has been found by DSC.

Besides confirming the EGA results, the FT-IR findings show unequivocally that $Na_2CO_3$ is present in the samples taken by DSC beyond the first endotherm. Incidentally, the behaviour of the intensity of the 880 $cm^{-1}$ band (Fig. 3b) parallels that of the initial endotherm, suggesting a possible use for quantitative determinations. The band observed at 849 $cm^{-1}$ in the spectra of the untreated Solvay samples (Fig. 3a) might suggest the presence on the crystal surfaces of small amounts of the double carbonate $Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$ formed during prolonged ageing; indeed, for this salt the internal mode of $CO_3^{2-}$ is at 851 $cm^{-1}$ [5]. Further information on the structural difference between the $NaHCO_3$ samples

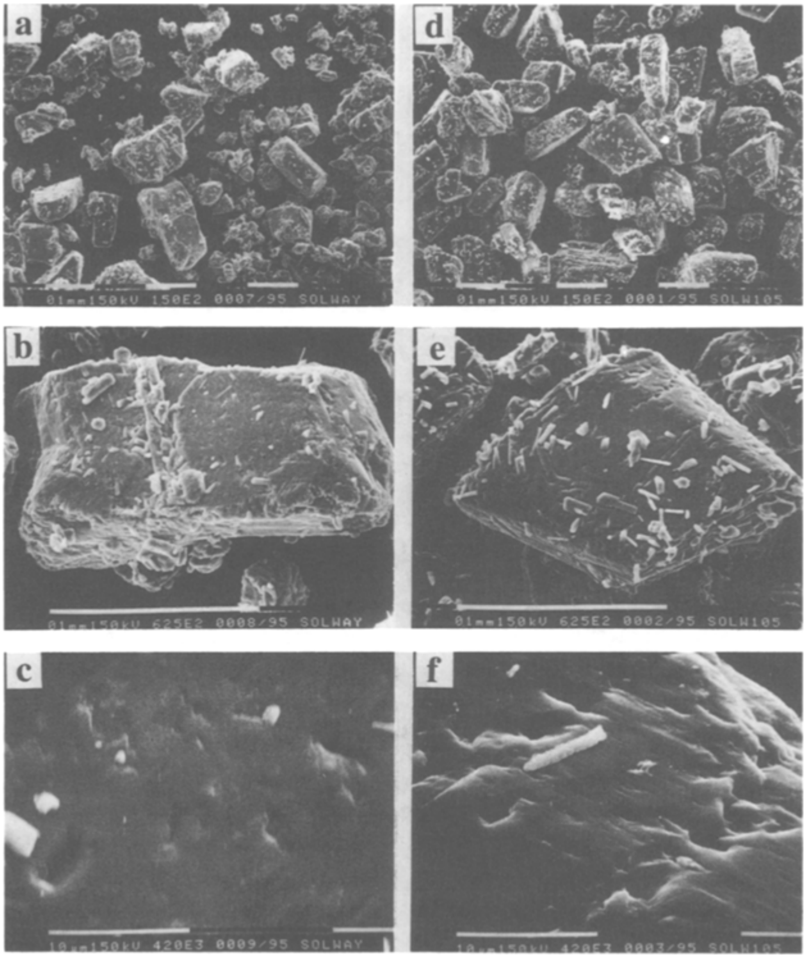

**Fig. 5** SEM micrographs of Solvay $NaHCO_3$ crystals (a, b, c) and of the same material taken to 105°C (d, e, f) at various magnifications

exhibiting the endothermal peak and those (not aged and/or not wet) which do not comes from the analysis of the spectra in the range of the –OH stretching (Fig. 4). It is impossible to correlate the band at 3470 $cm^{-1}$ (present for both the Solvay and the 80 or 90% *RH* DXt samples, i.e. for aged and wet materials) with some well-defined stoichiometric hydrate because of the identity of the other parts of the spectra with that of pure dried $NaHCO_3$. Thus, it appears plausible that ageing and/or crushing in a wet atmosphere results in a significant adsorption of water on the surface of the crystals.

The thermal results emphasize that mechanical treatment in wet atmospheres plays a dominant role in the initial part of the decomposition of $NaHCO_3$, but

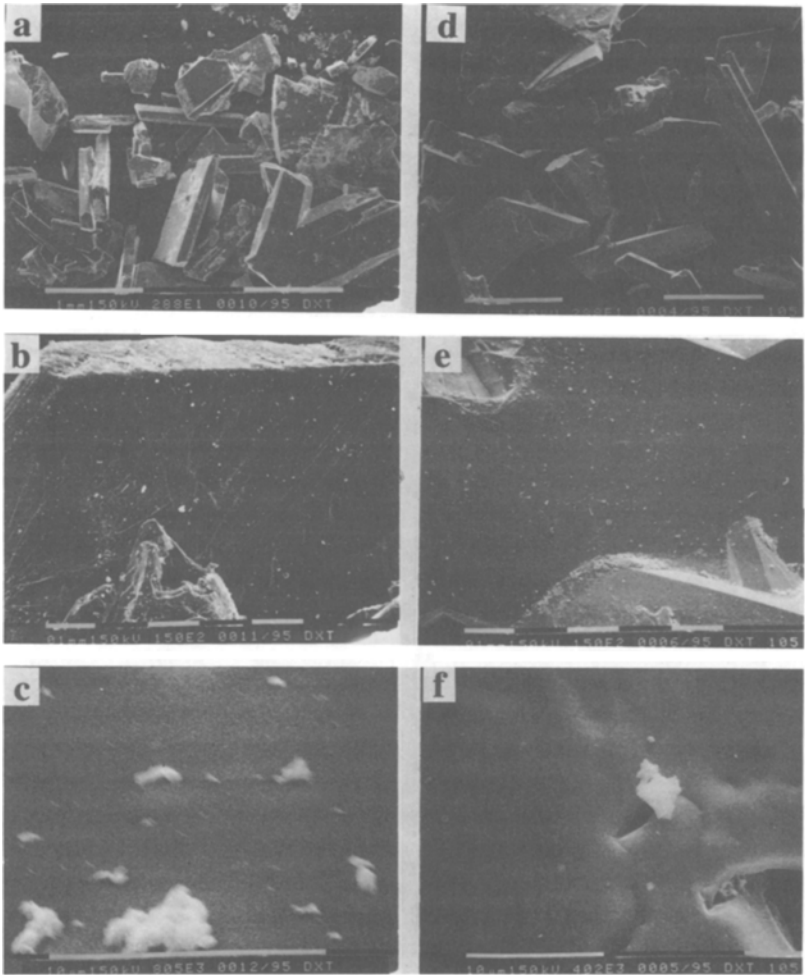

**Fig. 6** SEM micrographs of DXt crystals (a, b, c) and of the same material taken to 105°C (d, e, f) at various magnifications

some considerations are necessary for a plausible interpretation. A detailed analysis of the thermal results indicates that crushing alone has little effect on the subsequent thermal and kinetic behaviour; in fact, the data on the samples crushed in low *RH* match those previously obtained on uncrushed DXt. In contrast, grinding in high *RH* atmospheres is effective; this treatment leads to overall decompositions whose kinetic parameters resemble those typical of commercial samples (see, in particular, the Erba and Solvay samples in Table 2 in Ref. [1]). However, the shift in the whole thermal curve towards higher temperatures, typical of the WXt samples [1], remains. This indicates that, apart from the values of the kinetic parameters to be discussed later, the mechanical action at high *RH* results mainly in an amplification of the effects responsible for the low-temperature endotherm. Furthermore, the crushing experiments suggest that the adsorption of water on the surface of $NaHCO_3$ crystals is poor and probably also slow, unless relatively high partial pressures of $H_2O$ are used. As the EGA results on DXt (whose surface is almost devoid of water because of the nature of the storage and of the above considerations) indicate quite unambiguously that the preliminary endotherm can be attributed only to the decomposition of $NaHCO_3$, we conclude that in this step the surface layers of the crystals are decomposed to carbonate, whose presence after the first endotherm is confirmed by FT-IR.

On the other had, DSC experiments indicate that the considerably increased surface area brought about by crushing at low *RH* is not sufficient to render the apparatus sensitive to this decomposition, whereas the exposure of uncrushed crystals to local ambient atmosphere (*RH* sometimes higher than 60% and reaching 80% in exceptional circumstances) is (Fig. 1). Hence, water adsorption on crystal surfaces is the main factor responsible for i) the enhancement of the initial decomposition; ii) the shift in the whole thermal curves towards higher temperatures; both effects seem proportional to *RH*. As concerns i), the mechanical treatment results in fractures, which expose inner planes different from the previously prevailing {010} ones; in the presence of a water-rich atmosphere, this allows an otherwise difficult adsorption, probably conducive to a surface reconstruction [6] favouring the successive decomposition of the interphasal layer. It must be considered, however, that the data might also be taken as due to a Smith-Topley-like effect [7]. This is usually interpreted in terms of water-assisted crystallization of the dehydrated product [8, 9]; however, in the present case such an explanation appears untenable, as the simultaneous shift in the curves (ii) towards higher temperatures entails the formation of a protective layer retarding the evolution of the product gases and slowing down the transformation [1]. At variance with the findings in the previous paper, this layer, whose crystallization difficulties have already been demonstrated [1], is now envisaged as composed of amorphous (hydrated?) carbonate.

A comparison of the 90% *RH* thermal curve (Fig. 2) with the curve previously reported for WXt (Fig. 2 in [1]) indicates that in the present case the shift towards higher temperatures is less pronounced and that the peak is not so sharp. Both these differences can be ascribed to the mechanical treatment; in fact, crushing necessarily generates numerous (both surface and bulk) defects in the crystals. Some of these may be conducive to product crystallization [10], thereby making the protective layer not so effective as in the uncrushed WXt crystals. Furthermore, the reduced size of the crystals, coupled with the increased defectivity, necessarily facilitates the diffusion escape of the product gases. Taking into account the corresponding decrease in pressure of the inner gaseous products [11], the observed lowering of the activation energy is accounted for.

The SEM investigations on the Solvay crystals appear particularly interesting inasmuch as they reveal that the thermal treatment to 105°C affords nothing but the completion of a process already commenced during the ageing period (in fact, a comparison of Figs 5b,c with Fig 6e,f reveals that the surface of the untreated material already shows the presence of some corrugations, holes and small crystallites protruding from the inside). The latter features are lacking from the surface of DXt crystals (Fig. 6b,c), but they develop somewhat upon thermal treatment (undulations rather then corrugations, a few rather than several holes, and the scattered presence of crystallites; Fig. 6e,f). These findings shed light on the mechanism of ageing of $NaHCO_3$ crystal surfaces and support our previous interpretation of the shape of the thermal curves (highly defective surfaces correspond to relatively flat thermal decomposition curves because of the unhindered escape of the gaseous product), confirming the proposed mechanism of decomposition. Indirectly, the SEM findings also confirm the central role of water in promoting surface ageing. In fact, the decomposition to carbonate of surface layers of bicarbonate crystals kept in anhydrous atmospheres is demonstrated to be very poor.

## Conclusions

The main results of the present research can be summarized as follows:

i) EGA has shown that, independently of the kind of material used, the preliminary endotherm involves the simultaneous evolution of both water and $CO_2$;

ii) the FT-IR spectra reveal that commercial and high *RH* samples contain adsorbed and/or crystal hydrate water, and that the spectra of samples taken to temperatures higher than that of the first endotherm demonstrate the presence of a band, typical of carbonate, whose intensity parallels that of the preliminary endotherm;

iii) the DSC experiments indicate that the intensity of the low-temperature endotherm can be enhanced by crushing in high *RH* atmospheres and is proportional to the *RH*; such mechanical treatment makes the thermal curves shift towards higher temperatures and lowers the activation energy of the main decomposition process;

iv) the SEM experiments confirm the EGA and DSC findings and provide detailed information on the ageing of crystal surfaces; at the same time, they ensure the validity of the mechanism proposed in the previous report for the overall decomposition.

These new results lead to a new explanation of the preliminary endotherm: the new findings indicate that what takes place during that thermal event is the water-assisted decomposition of the surface portions of the crystals to a layer of (probably) amorphous carbonate. This does not exclude, however, a minor contribution due to dehydration of hydrated carbonate already present [1], particularly in the case of commercial samples stored for a long time. The type of mechanism previously envisaged for the main decomposition remains unchanged, however, and the lowering of the activation energy of decomposition of high *RH* samples is attributed to the easier diffusivity of the gaseous products generated by the reaction in the bulk.

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