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THE THERMAL DECOMPOSITION OF $NaHCO_3$ POWDERS AND SINGLE CRYSTALS

A study by DSC and optical microscopy

G. G. T. Guarini, L. Dei and G. Sarti

Lab. of Physical Chemistry of Interphases, Department of Chemistry, University of Florence,
Via G. Capponi, 9–50121 Firenze, Italy

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Abstract

The thermal decomposition of four commercial powders and of differently stored single crystals of sodium hydrogen carbonate is studied by power compensation DSC and by optical and FT-IR microscopy. Independently of manufacturer, specified purity and price, the thermal curves of all the commercial powders show a more or less pronounced low temperature peak preceding the one due to the main decomposition. Such small peak is not observed when samples of laboratory recrystallized material are used. However the thermal behaviour of the latter preparation differs remarkably depending on storage conditions: the material kept in closed glass containers decomposes at temperatures higher than those of the material stored in a dessiccator in the presence of concentrated H_2SO_4.

The observation by optical microscopy of the behaviour of the surfaces of single crystals coming from different storage conditions when the temperature is raised in a Kofler heater helps the interpretation of the data collected.

The mechanism of the decomposition is discussed and the relevant kinetic parameters reported.

Keywords: DSC, single crystals, sodium hydrogen carbonate

Introduction

Sodium hydrogen carbonate has domestic and pharmaceutic uses; its thermal decomposition has relevant industrial importance (Solway process) and was repeatedly studied [1–5].

Years ago the thermal decomposition of $NaHCO_3$ (believed a typical first order process) was used in these labs to test the dependence of the kinetic parameters deduced from thermal curves on the mass of the sample [6]. Our renewed interest in this reaction comes from the wish of testing, in chemical changes other than dehydrations of salt hydrates [7–13], our point of view about the role of crystal interphases on the mechanism of decomposition reactions.

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Literature search encouraged the undertaking of this work; indeed Ball *et al.* [3], using an A.R. grade material, found evidence of the early formation of a surface layer with texture differing from the material underneath. This suggested that a decomposition behaviour similar to the one found for nickel sulphate hexahydrate [14] and alums [15] might be effective also in this instance. Furthermore very recently Tanaka and Takemoto [5], using reagent grade material, have reported that even if the samples show order of reaction type kinetics, the particles constituting the samples decompose according to a $n = 2–3$ contracting envelope kinetics. This is here considered an indication that the interfacial zones of the crystals may play a role in the transformation.

The thermal decomposition of $NaHCO_3$ takes place in a single step according to the stoichiometric equation:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

However Barrall and Rogers [1] reported the presence of a minor endothermal event preceding the main decomposition peak and attributed it to the simple decomposition above. This again encouraged us to choose this compound to test our hypotheses. In fact the minor endotherm have been due to a differentiated reactivity of the surface zones of the crystals with respect to the bulk ones [16].

Experimental

The four sodium hydrogen carbonate powders: Solway for domestic use, Erba F.U. (F.U.=Official Pharmacopoeia), Merck 99.5% pro analysi (Merck PA) and a relatively expensive Merck special preparation for *pH* standard buffer solutions (Merck**) were used without further treatments. Single crystals were obtained, according to Pascal [17], by dissolving (at temperatures ≤45°C) the Merck P.A. product in doubly distilled water and allowing the solutions to cool to room temperature (ca. 22°C). The resulting crystals were recovered from the solution and dried using soft filter paper and a flow of dry nitrogen before storing them, in air, in part (DXt) in a desiccator over conc. H_2SO_4 and part (WXt) in a glass test tube closed by a plastic stopper. Microscopic observation revealed that the recrystallized material was constituted mainly of (millimeter length) thin needle-like crystals exposing relatively large {010} planes (as stated with reference to Groth [18]).

The thermal curves were evaluated by means of a Perkin-Elmer (PE) DSC 7 power compensation differential scanning calorimeter equipped with PE pc software and used mainly in the non-isothermal mode, with a dry nitrogen flow of 16 $cm^3 \cdot min^{-1}$ purging the apparatus cell. The scanning rates (β) employed ranged from 0.2 to 16 $deg \cdot min^{-1}$. However the calibration of the apparatus was performed at $\beta = 5$ through the meltings of biphenyl and tin and tested with the

NH_4NO_3 125°C transition and the melting of indium [19]. The $NaHCO_3$ samples were weighed (ca. 10 mg) in the standard aluminium sample pans both before and after the thermal experiments. To evaluate the sample weight loss at intermediate temperatures some experiments were deliberately interrupted and then either restarted or not. Lids were invariably used to cover loosely both sample and reference pans thus matching the thermal emissivity [20]. For comparison some decompositions were also performed using a Mettler TA-2000 heat flux thermal analyzer. Kinetic analysis of the thermal curves was performed both using the PE software and, evaluating the fractional decomposition α and $d\alpha/dT$ at various temperatures, by the differential method [21]; in some instances the results were also favourably tested by the data treatment suggested by Malek [22].

Optical microscopy determinations were performed by using, mainly in the reflexion mode, a Reichert Zetopan microscope equipped with interference contrast, with a Kofler hot stage and with an Olympus OM2 camera. When necessary a cell already described [8] was also employed. The alimentation of the Kofler heater was regulated to obtain a temperature increase of about 5 deg·min^{-1} in the range of interest (60–170°C). Beyond the value read on the stage thermometer the temperature was monitored by a copper/constantane thermocouple junction placed in the immediate vicinity of the observed crystal on the supporting glass slide.

The surface area of the commercial powders was evaluated roughly by optical microscopy and the results compared with those obtained using low temperature adsorption of N_2/He mixtures in a Micromeritics Flow-Sorb II apparatus.

An EDT OAS 400 MK II photoacoustic spectrometer was used to record spectra in the near IR region of the original or partially decomposed materials at various chopping frequencies to gain evidence of the existence of a surface layer differing from the bulk material [12, 14, 15]. Possible modifications between differently stored single crystal materials were also sought by a FTS-40 Bio-Rad FT-IR spectrometer equipped with Bio-Rad UMA 500 microscope used mainly in the microreflectance mode in order to avoid possible surface damages caused by pelleting with KBr.

Results

Thermal evaluations

The typical thermal curve recorded at $\beta = 5$ for the decomposition of a 10 mg sample of the Merck** product is reported in Fig. 1a. A small endotherm preceding the main one is clearly evident but the onset temperature

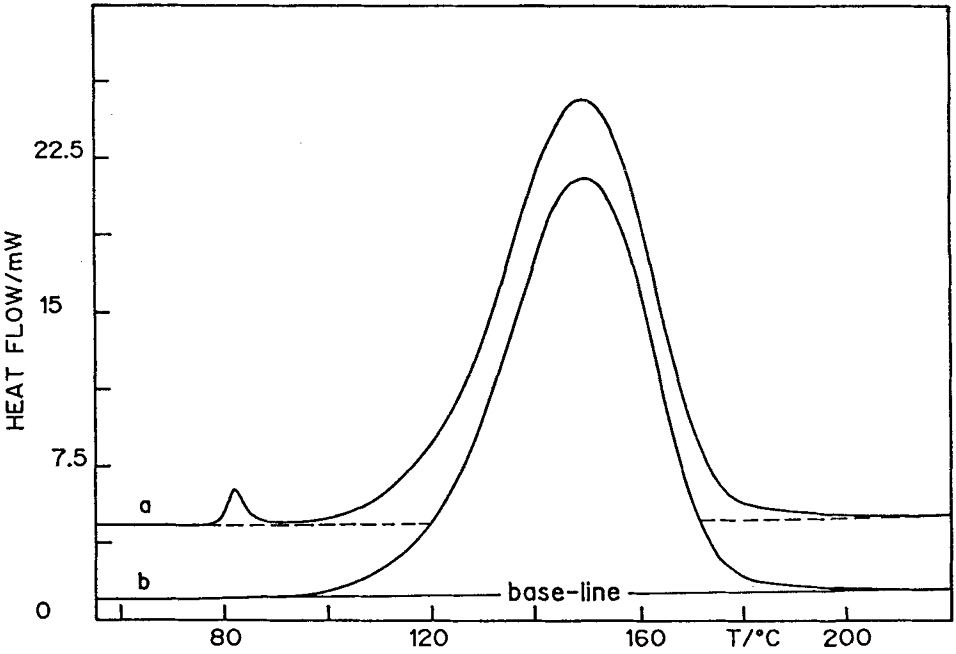

Fig. 1 Thermal curves for the dehydration of commercial crystalline powders of $NaHCO_3$: a) as received; b) samples that had previously been heated up to the completion of the low temperature peak

(extrapolation to the base-line of the leading edge of the peaks), ca. 83°C at $\beta = 8$, is much lower than that reported by Barrall and Rogers (111.8°C at $\beta = 7.9$) for their first endotherm [1]. Similar thermograms were recorded for the other commercial products, the main difference lying in the size of the small initial peak. Value for the onset temperatures and enthalpic changes connected with both the first peak and the main decomposition endotherms are collected in Table 1 for all the commercial products and for the differently stored recrystallized material used. The heat data reported refer either to experiments performed at $\beta = 5$ (columns b, c, d, e) or to averages over the whole range of β (column f). In the same table (column g) the mean values of the percentual weight losses after complete decomposition (for comparison with the theoretical value of 36.92%) as well as the approximate values of the surface areas of the commercial powders (final column) are reported.

In some instances the runs of the commercial products were interrupted after the first peak and the weight losses determined, these resulted approximately 1% of the total weight loss with some variations depending on the commercial material used. Performing new experiments with the residues of the runs interrupted after the first peak originated thermal curves of the shape reported in

Table 1 Thermal data

Material	Onset I/°C	ΔH^{I} / J·g^{-1}	Onset D/°C	ΔH^{D} / J·g^{-1}	$\Delta H^{\#}$ / J·g^{-1}	ΔW%	Area/m^2·g^{-1}
Erba F. U.	79.2±0.4	13.5±1.0	111.4±2.2	800.4±49.8	805.1±49.8	36.49±0.10	0.101
Merck P. A.	75.9±0.6	5.1±0.3	113.5±1.4	793.8±20.3	759.1±80.1	36.51±0.19	0.124
Solway	81.6±0.3	6.9±0.4	114.8±2.1	795.6± 6.5	789.2±21.3	36.44±0.19	0.106
Merck**	78.9±0.4	8.2±0.6	119.5±2.5	798.8± 7.9	787.6±47.1	36.45±0.20	0.138
DXt	–	–	133.9±3.9	796.3±10.7	794.8±16.3	36.78±0.12	–
WXt	–	–	139.9±3.3	811.1±17.1	807.3±23.2	36.75±0.20	–
Mean Values		8.4±3.6	–	799.4±21.9	790.5±63.9	–	0.117±0.02

I = First peak at $\beta = 5$

D = Main Decompoisiton at $\beta = 5$

$^{\#}$ = Main Decomposition, mean values over whole range of β

Fig. 1b (Merck**, $\beta = 5$) in which the low temperature peak is absent but the shape of the main decomposition endotherm is almost unchanged when compared with the one in Fig. 1a.

In Fig. 2 the thermal curves for the decomposition at $\beta = 5$ of ca. 10 mg samples of DXt (full line) and WXt (broken line) coming from the same recrystallization batch are reported. The remarkable differences between the two curves are clearly evident {e.g. the decomposition of WXt takes place at higher temperatures, has an evident initial shoulder at temperatures somewhat higher than the first endotherm of Barrall and Rogers [1], is steeper and shows a high temperature tail attributed to retention of the gaseous products}. A comparison with Fig. 1a evidences the absence of the initial small peak for both WXt and DXt; the shape of the endotherm of DXt samples agrees better with the curve in Fig. 1b but the whole curve is shifted to higher temperatures.

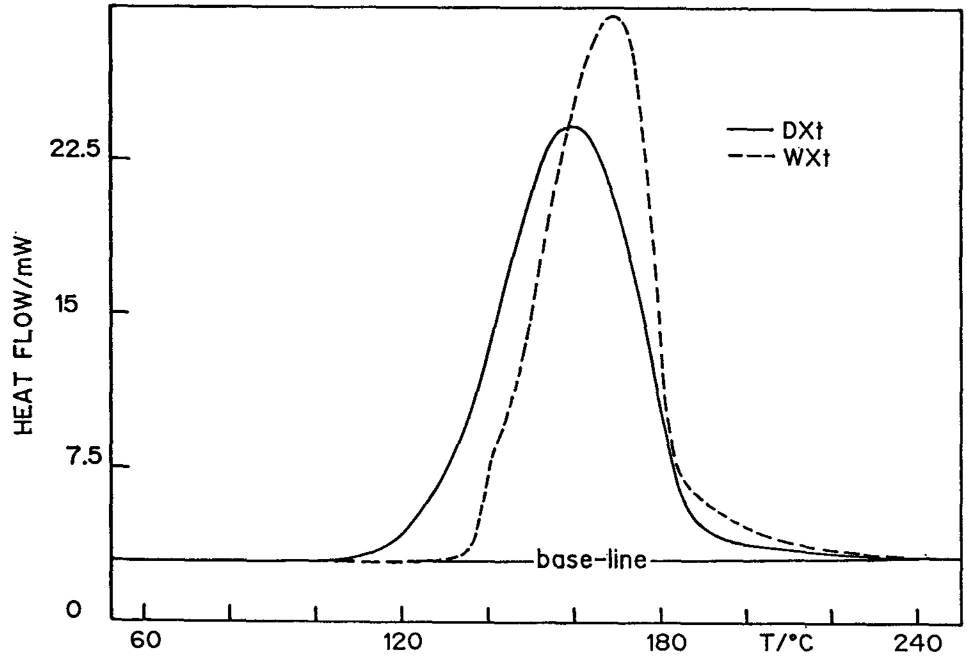

Fig. 2 Thermal curves of differently stored crystals of $NaHCO_3$ (see text)

Including or excluding the small initial peaks had no effect on the evaluation of kinetic parameters from the thermal curves. In Table 2 the mean values of activation energies (E_a), preexponential factors (ln$A$) and reaction order (n) are collected as deduced from PE software. In the same table the values of the kinetic parameters, evaluated by the differential method using the first order equation (found to be best fitting), are reported; furthermore the values of E_a

Table 2 Kinetic parameters

Material	P. E.			Differential (n = 1)		Ozawa
	ln$A$/min^{-1}	E_a / kJ·mol^{-1}	n	ln$A$/min^{-1}	E_a / kJ·mol^{-1}	E_a / kJ·mol^{-1}
Erba F. U.	24.5±1.8	103.5± 5.8	1.30±0.05	23.8±1.8	93.1± 4.4	107.3±2.1
Merck P. A.	27.8±1.5	114.0± 4.6	1.11±0.09	27.3±1.5	106.1± 5.8	106.8±5.1
Solway	26.9±2.1	111.4± 4.6	1.17±0.08	25.9±0.8	101.5± 1.8	104.6±4.3
Merck**	28.1±2.4	116.7± 7.8	1.13±0.10	28.6±1.3	109.5± 5.3	116.7±3.3
DXt	26.7±2.2	116.2± 7.8	1.08±0.14	27.1±2.1	109.9± 8.4	100.8±3.4
WXt	32.9±2.7	139.5± 9.9	0.93±0.06	35.2±3.8	138.6±12.9	122.3±7.4
Mean Values	27.8±2.8	116.9±12.1	1.10±0.09	28.0±3.9	109.8±15.4	109.7±8.1

obtained from the multiple scan Ozawa [23] method are tabulated for the sake of comparison. The isoconversional method [22] employed at six α values (0.1, 0.2, 0.4, 0.6, 0.8, 0.9) gave comparable values for E_a and proved its independence of α. This is often considered indicative of a single decomposition mechanism.

Optical microscopy

Two sequences of micrographs obtained during the heating in the Kofler stage of single crystals of DXt and WXt are reported in Figs 3 and 4 respectively. Both sequences show an important common feature, namely that the crystals undergo cracking as first consequence of temperature increase. It is clearly evident however that in the case of WXt a sort of nucleation of the observed surfaces takes place. Comparison of the temperatures indicates correspondence of this surface retexturing with the shoulder of the WXt endotherm. Such behaviour is not shown by DXt crystals whose surfaces remain unaltered up to complete decomposition. This remarkable difference of behaviour between DXt and WXt crystals parallels the one found in thermal behaviour (Fig. 2).

FT-IR microscopy and Photoacoustic spectrometry

In Fig. 5 the FT-IR spectra of DXt and WXt are reported for comparison. The two spectra look identical so that the two samples do not show significant changes of the surface structure, at least in the IR region 800–4000 cm^{-1}.

Probably because the limited sensitivity of the photoacoustic spectrometer in the near IR region did not allow a sufficient change in the chopping frequency, the differences observed in the spectra recorded made impossible to safely assess the existence (or the formation after partial decomposition) of a surface layer in the materials studied.

Discussion

Commercial products

If we exclude the report by Barrall and Rogers [1] none of the thermal studies on the decomposition of commercial sodium hydrogen carbonate here examined indicated the presence of a small endotherm preceding the main decomposition. According to Pascal [17] 'In wet air, the salt loses slowly carbonic gas, fixes some water and transforms into hydrated neutral carbonate'. This suggests that commercial products, because of long storage, have under-

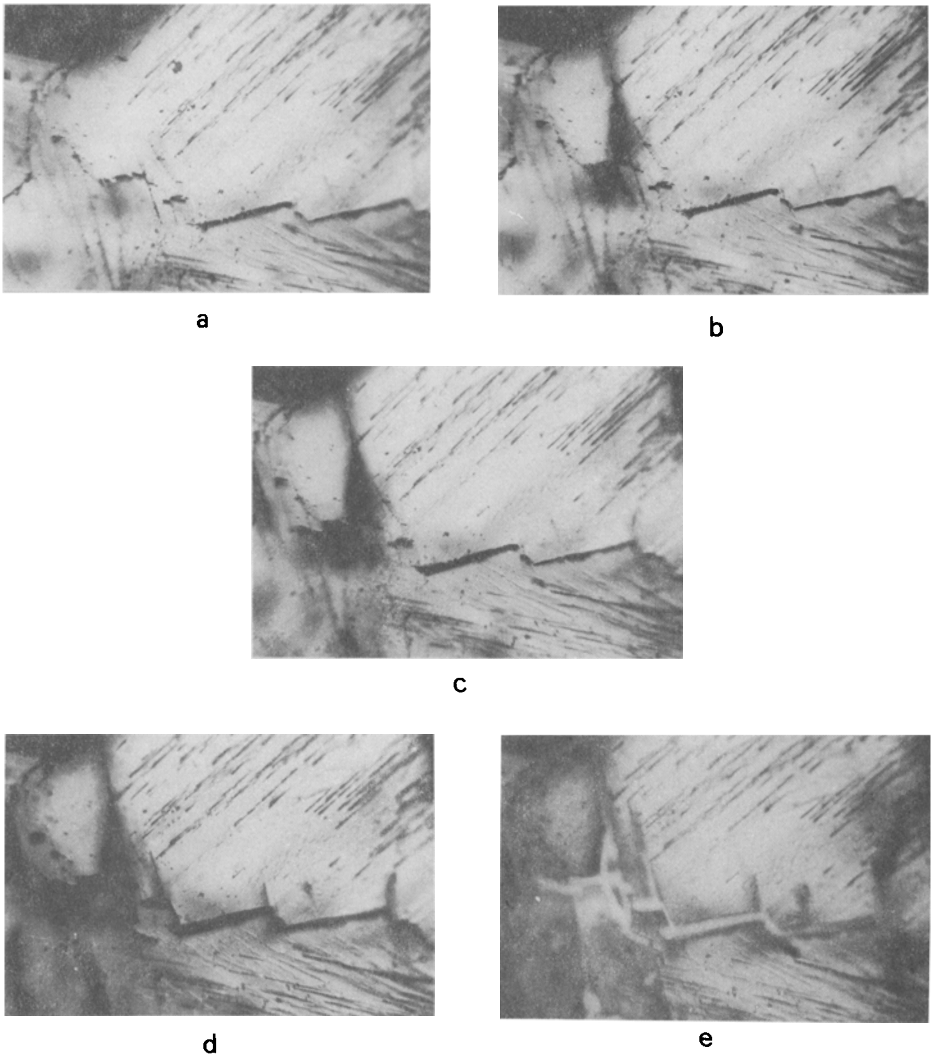

Fig. 3 Sequence of micrographs of the decomposition of a DXt crystal: a) room temperature; b) 105°C; c) 118°C; d) 135°C; e) 154°C. Cracking is evident in b)

gone some superficial transformation to neutral carbonate hydrated whose dehydration is the responsible of the small low temperature endotherm preceding the decomposition one. To the same phenomenon is probably due the small deviation from stoichiometric loss ascertained by weighing. From the overall weight loss the commercial samples appear to have almost the same purity. As they have also comparable surface areas, it appears that the fraction transformed in carbonate on surfaces is approximately equal for all samples (i.e. the superficial

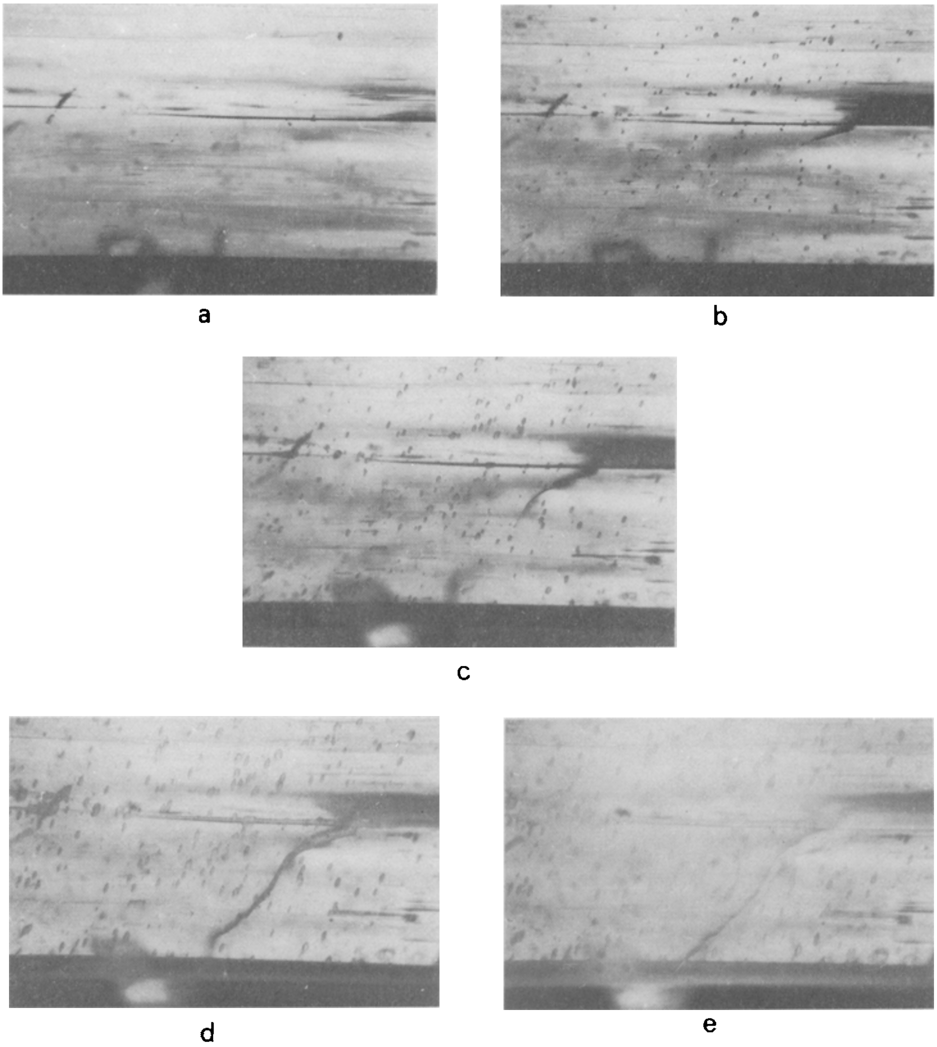

Fig. 4 Sequence of micrographs of the decomposition of a WXt crystal: a) 85°C; b) 134°C; c) 139°C; d) 150°C; e) 162°C. Also in this case cracking is evident in b)

transformation penetrates always the same depth). The observed differences in extent of the small first peak (irrelevant with respect to the global event) are then attributed to changes in the degree of hydration of the product carbonate. This indicates the sequence: Erba F.U.>Merck**>Solway>Merck P.A. The relatively high value of the heat associated with the first peak of the Erba samples induces to suspect the presence of ammonium carbonate as impurity.

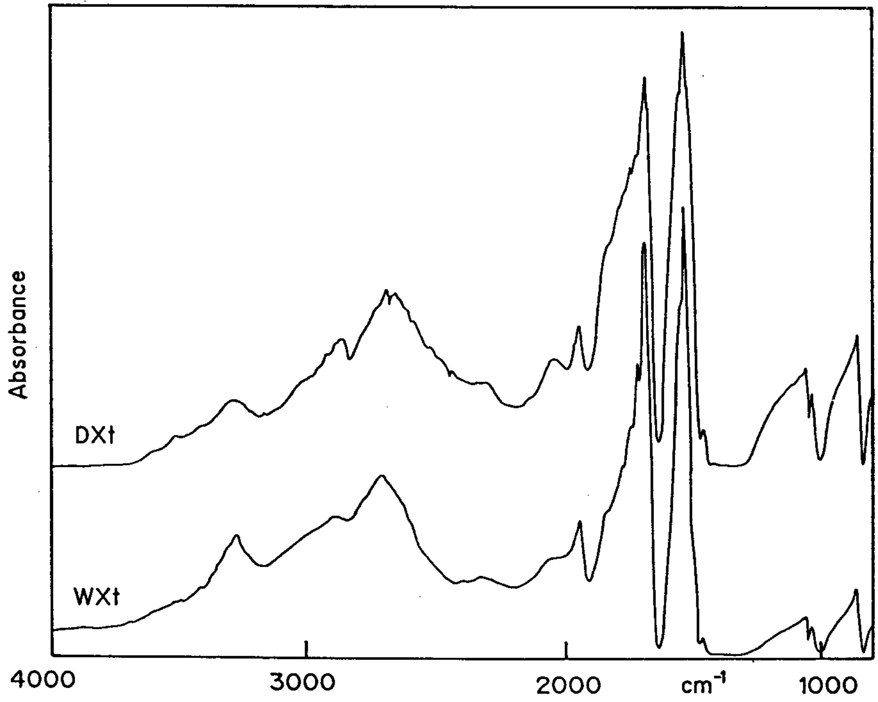

Fig. 5 FT-IR microreflectance spectra of DXt and WXt crystals, no significative differences are observed

Once the initial dehydration of superficial carbonate has taken place, the solid reaction product is already present on the surfaces of the microcrystals constituting the commercial powders so that surface nucleation cannot be expected to play any role in the kinetics of the subsequent decomposition. By analogy with the dehydration reactions of salt hydrates, the previously reported deceleratory rate laws appeared then justified. Furthermore the same surface process was expected almost 'to equalize' the samples of different origin with respect to the successive transformation. This resulted only partly true, in fact if in the various experimental conditions the different samples showed all first order kinetics, the kinetic parameters deduced varied somewhat suggesting that other properties (e.g. defect content, etc.) could play some role. This was the first indication that, at variance with a good number of dehydrations, in the present system the reaction occurred in the bulk. This was confirmed by the work on single crystals (see below).

Recrystallized material

The main differences among the thermal curves of commercial and recrystallized materials have been evidenced previously, also the different behaviour of DXt and WXt has been noted, we can note here that the weight loss is almost stoichiometric both for WXt and DXt. In spite of the above (in some cases remarkable) differences, all kinds of kinetic analysis of the peaks confirm first order obedience in all instances; furthermore invariance of E_a with α suggests that a single mechanism is operating. This requires some considerations.

Our findings by optical microscopy prove that lattice collapse, transforming the crystals into a collection of singularly decomposing microcrystals (first order process [24]), can be considered the real responsible of kinetic obedience. Proof of lattice collapse comes from the evidenced cracking of single crystals and from the observed increase in light diffusivity blurring somewhat the final frames of Figs 3 and 4.

We believe that reaction taking place in the bulk originates lattice collapse. Direct evidence of inner reaction comes from Fig. 3 showing that the surface remains unaltered up to almost complete decomposition. Indirect evidence can be drawn from Fig. 4c, d, e by analogy with the dehydration of α-$NiSO_4 \cdot 6H_2O$ [14], in fact also in the present instance the surface nuclei do not grow significantly while the transformation goes to completion indicating inner reaction.

The above interpretation entails the presence of a surface layer poorly permeable to the gaseous reaction products. As described in the experimental part our attempts to gain independent evidence of such a layer failed. However optical and thermal experiments on WXt are fundamental in this respect. In fact in this case the transformation takes place at high temperature and is characterized by high activation energy that can be attributed to high product pressure at the reaction site [25]. These findings are here considered evidence of the existence of a poorly permeable surface layer. Further proof can be considered the observed nucleation of WXt surfaces in fact, according to recent interpretations [7, 13–15], the nucleus is the site where crystallization of already formed product takes place and this requires the initial transformation of a superficial layer. We recall that a superficial layer was described also by Ball *et al.* [3].

While the sudden departure from the baseline of the WXt endotherm is another indication of surface hindered inner reaction, the shoulder observed in the initial part of the main peak of WXt samples, roughly corresponding to the first endothermal event found by Barrall and Rogers [1], testifies surface decomposition of a protective layer of hydrated bicarbonate formed on the surfaces of crystals because of their permanence in wet air. (On longer exposure to humidity such a layer is probably conducive to the superficial decomposition described by Pascal [17] and characterized by the presence of the small initial dehydration peak.) Almost at the same time product crystallization (nucleation) takes place on the surface. These events remove at least partially the superficial impermeability and the reaction takes place rapidly (steep peak).

The transformations of commercial materials and of DXt do not show thermally such surface dependence and apparently take place regularly as decaying processes. But microscopy reveals that cracking takes place in DXt indicating presence of inner reaction and lattice collapse also in this case. The surface film however must be much more permeable than the one formed on WXt (probably because the crystal surfaces are deprived of water) so that the reaction takes place regularly and the inner pressure does not increase the activation energy. The increase in the decomposition temperature of DXt with respect to the commercial materials is attributed to the absence, on DXt surfaces, of product crystallites (nuclei) generated by the dehydration of the superficial carbonate (Pascal [17]) and altering the continuity of the surface layer of the crystals. Microscopic evidence, confirming that nothing particular happens on the surfaces during decomposition, indicates that reaction takes place mainly in the bulk; first order obedience is again interpreted in terms of the proportionality of rate to the number of residual reactant crystallites [24].

Conclusions

The present work shows that the decomposition of $NaHCO_3$ is affected by storage conditions. Evidence is found that, at variance with a good deal of thermal dehydrations (starting on crystal surfaces) the decomposition of sodium hydrogen carbonate initiates in the bulk causing lattice collapse and subsequent first order kinetics. The activation energy of the process is however affected by the presence of a poorly permeable layer of hydrated material that forms on the surfaces of the crystals (WXt crystals and commercial materials) by storage in wet air.

Even if in the present instance the photoacoustic or the FTIR techniques did not give the expected independent evidence of differences in the nature of such surface layers on original or partially reacted materials, nevertheless we believe that the present findings are sufficient to prove that also the mechanism of the thermal decomposition of hydrogen carbonate is strongly dependent on the properties and behaviour of the outer parts (i.e. the interphasal layer) of the crystals. This encourages us to further work on the role of the interphasal zones in the reactivity of solids studying decompositions of various crystalline materials in view of a possible generalization of our ideas.

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Zusammenfassung — Mittels Leistungskompensations-DSC sowie mittels optischer und FT-IR Mikroskopie wurde die thermische Zersetzung von vier handelsüblichen Pulvern und verschieden gelagerten Einkristallen aus Natriumhydrogenkarbonat untersucht. Unabhängig von Hersteller, angegebener Reinheit und Preis zeigen die thermischen Kurven aller handelsüblichen Pulver einen mehr oder weniger ausgeprägten Niedertemperaturpeak, der demjenigen für die Hauptzersetzung vorangeht. Werden Proben aus im Labor umkristallisierten Material verwendet, können derartig kleine Peaks nicht beobachtet werden. Auf alle Fälle unterscheidet sich das thermische Verhalten letzterer Darstellungsmethode bedeutend, je nach Lagerungsbedingungen: Substanzen in verschlossenen Glasbehältnissen zersetzen sich bei einer höheren Temperatur als Substanzen, die in einem Exsikkator in Gegenwart von cc.H_2SO_4 gelagert wurden.

Die Beobachtung des Verhaltens der Oberfläche von Einkristallen aus verschiedenen Lagerungsbedingungen mittels Lichtmikroskopie in einem Kofler-Mikroskop bei steigender Temperatur unterstützen die Interpretation der gesammelten Angaben.

Der Zersetzungsmechanismus wird diskutiert und die relevanten kinetischen Parameter beschrieben.