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Kinetics and mechanism of the thermal dehydration of *l. asparagine* monohydrate microcrystals and single crystals: Role of ageing

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Abstract

In an attempt to extend studies on the dehydration reactions of crystal hydrates from the inorganic to the organic field, the dehydration of *l. asparagine* monohydrate crystalline powders and single crystals was studied using isothermal and dynamic power compensation DSC as well as optical and FT-IR microscopies. The dehydration was strongly dependent upon the ageing of prepared crystals. Furthermore, crystals obtained by evaporation of solutions containing 30% methanol behaved differently.

The kinetics of the overall dehydration results were independent of ageing and were characterised by obedience to the Avrami–Erofeev (n=3) law in isothermal runs at low and medium temperatures while, at the highest temperatures, first-order equations resulted in the best fit. In dynamic scans, order-of-reaction type laws gave the best fit and a dependence of the kinetic parameters on temperature gradient was ascertained.

Optical microscopy revealed that the final textures of the surfaces of dehydrated crystals, depending on whether the reaction took place isothermally or not, differed. Moreover, non-isothermal runs performed under the microscope, at rates of temperature increase comparable with those used in DSC, revealed surface corrugation due to internal pressure generated by gaseous products as well as the presence of liquid phases.

Micro-reflectance FT-IR spectra showed that dehydration started in the outer surface layers. These findings are typical of systems whose kinetics and mechanisms of decomposition are dominated by the properties of the outer boundaries of the crystals.

The results are discussed in terms of a three-stage mechanism and a model accounting for these reactions is proposed. The relevant thermal and kinetic parameters are reported. © 1998 Elsevier Science B.V.

Keywords: Crystal decomposition; DSC; FT-IR; Kinetics and mechanism; *l. asparagine*; Thermal dehydration

1. Introduction

This study set out to verify if our interpretation of the kinetics and mechanism of dehydration of a large number of inorganic crystal hydrates by a three-stage mechanism (TSM) [1–4] could be extended to organic crystal hydrates. The TSM is characterized by

(i) an initial dehydration of the outer lattice planes to form a dehydrated layer;
(ii) diffusion of the volatile reaction product through this layer; and

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(iii) formation of crystalline germs of the product in the dehydrated layer.

Experiments on organic crystals were also considered to be of relevant interest in making a plausible interpretation of some anomalous results obtained from studies on the dehydration of sodium citrate dihydrate [5]. This paper refers to studies, lasting more than two years and performed using various experimental techniques, on the dehydration of fresh and aged crystalline powders and single crystals of *l. asparagine* monohydrate.

l. asparagine monohydrate (LAM) crystals pertain to the $P2_12_12_1$ space group with a=5.593 Å; b=9.827 Å; and c=11.808 Å and four molecules in the unit cell [6]. Their morphology was described by Groth [7] and Wang et al. [8] but can be modified by adsorption at specific crystallographic planes of "tailor made" solvents [9] or additives [8]. The nature of radicals formed upon irradiation with X-rays has been determined [10] and the kinetics of their decay seem to be related to the dehydration rate. A study of the thermal dehydration of asparagine crystals has been reported by Kalis et al. [11], indicating that water of crystallization is held more strongly than adsorbed water and suggesting a contracting envelope mechanism. This indicated that LAM crystals were particularly suitable for our purpose, in fact, in this study, a contracting mechanism entails the presence of a surface layer, a point that characterizes the TSM. Moreover, the possibility of modifying the crystal habit [8,9] and, hence, the kind of outer surface, seemed to offer great possibilities to investigate their role in the kinetics and mechanism of decomposition.

2. Experimental

2.1. Materials

The Merck *l. asparagine* monohydrate (LAM) was used for analysis, either untreated (*aged powder*) or dissolved in water (resistance ≥18 MΩ cm) that was purified with a MilliRO 6 and a Milli-Q water system (Organex system) at temperatures lower than 35°C [12] to prepare, by slow evaporation at room temperature, recrystallized small (0.05–0.2 mm size) or single (up to cm size) crystals (*crystals*) to be used for optical and FT-IR microscopy experiments. Small crystals (0.1–0.3 mm size), differing in habit, though not so dramatically as in [8,9], were obtained by slow evaporation of aqueous solutions containing 30% methanol [8] (*methanol crystals*) at room temperature. Once recovered from the solutions, the crystals were partially dried by gently rubbing with soft filter paper. The drying was completed in a dry atmosphere overnight. The crystals were then separately stored in glass test tubes closed with plastic stoppers.

2.2. DSC technique

A DSC Perkin–Elmer DSC7 differential scanning calorimeter (calibrated with biphenyl, indium and tin) was used to record thermal curves either isothermally or at various heating rates in the 0.1–16 K min^{-1} range. The samples (5–12 mg in dynamic runs and 15–20 mg in isothermal runs) were weighed in the standard aluminium sample pans and loosely covered with aluminium lids to balance possible thermal emissivity differences between sample and reference [13]. Repeated weighing after the runs allowed the evaluation of the amount of water lost and the determination of the reaction stoichiometry. A dry nitrogen flow of 16 ml min^{-1} was used to purge the calorimeter cell; in isothermal runs (55–80°C range) the nitrogen flow was started only when the sample had reached the required temperature. Non-isothermal runs (40–180°C range) were performed at various heating rates in the 0.1–16 K min^{-1} range. The kinetic analysis of the isothermal runs was performed by determining which of the several solid-state rate equations, relating fractional decomposition (α) and time [14], gave the best fit to the experimental findings. To avoid the unwanted interference of some spikes, often present, the kinetic analysis of dynamic thermal curves was limited to the initial main dehydration peak (i.e. to the initial 75–85% decomposition for *crystals* and *methanol crystals* and 92–95% decomposition for *aged powder*) and was performed either directly by means of the Perkin–Elmer software or by extracting α and $\mathrm{d}\alpha/\mathrm{d}T$ values from the recorded data and using the method reported in [15] and employed previously [1–5].

2.3. FT-IR technique

FT-IR spectra of the various kinds of LAM as well as of dehydration residues were collected, after pelletization with KBr, using a Bio-Rad FTS-40 FT-IR spectrometer. Microreflectance spectra of single-crystal specimens were recorded by means of the associated Bio-Rad UMA 500 microscope, the temperatures of the crystals being changed by means of a Peltier heating support. The sample compartments were purged with dry nitrogen.

2.4. Optical microscopy

The dehydration of single crystals of LAM was also studied by optical microscopy using a Reichert Zetopan microscope equipped with interference contrast, hot stage and an Olympus OM2 camera. To reproduce most closely the conditions of the samples inside the DSC, a cell was employed [16] in which the same flow of dry nitrogen was used to feed the DSC. The temperature inside this cell (as well as that on the hot stage) was checked by means of copper–constantan thermocouples positioned very near the crystal under examination. Almost constant rates of temperature increases (of the same order as those used with DSC) could be realized by careful adjustment of the current flowing in the heating resistances.

3. Results

3.1. Thermal evaluations

3.1.1. Isothermal runs

Three thermal curves recorded, on a 20-h basis, at 70°C, using *aged powder*, aged *crystals* and *methanol crystals* are presented in Fig. 1. Relevant differences are evident concerning the rate of the processes, as deducible from the shape of the thermal curves, that result in the following order:

aged powder > *crystals* > *methanol crystals*

Evaluation of the enthalpic changes indicates that the heat of transformation for *aged powder* (ΔH=61.6±2.6 kJ mol^{-1}) and for *crystals* and *methanol crystals* (ΔH=66.9±3.4 kJ mol^{-1}) appear rather high if compared with those common to most inorganic crystal hydrates (ca. 55 kJ mol^{-1}), but seem in line with previous findings [11]. Within the experimental errors the amounts of water loss always seemed to be in agreement with the stoichiometry of the following reaction:

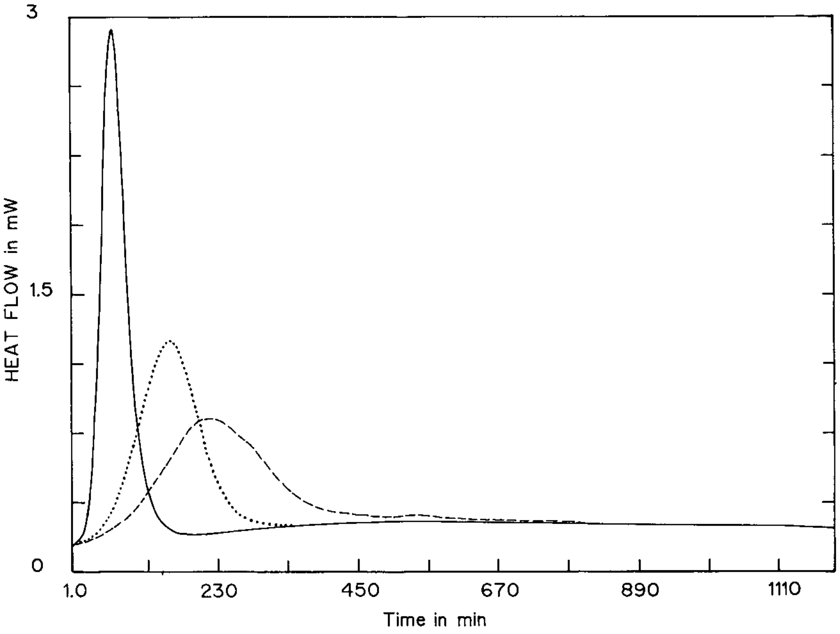

Fig. 1. Isotherms obtained at 70°C of the different LAM preparations: solid line, *aged powder* (19.3 mg); dotted line, *crystals* (19.22 mg); and broken line, *methanol crystals* (19.04 mg).

$$l.\ asparagine \cdot H_2O_{(solid)} \Rightarrow l.\ asparagine_{(solid)} + H_2O_{(gas)}$$

Kinetic analysis of the curves, performed as described previously [1–5,15], indicated as best fitting the n=3 Avrami–Erofeev equation. For runs at $T \geq 70°$, particularly for *aged powder*, first-order kinetics gave a better agreement. The kinetic parameters, evaluated from Arrhenius figures are: E_a=136.1±11.8 kJ mol^{-1} and ln (A/s^{-1})=40.3±4.2 for *aged powder*; E_a=159.1±12.3 kJ mol^{-1} and ln (A/s^{-1})=47.2±5.1 for young *crystals*; E_a=184.9±16.7 kJ mol^{-1} and ln (A/s^{-1})=51.7±5.5 for 2-year old *crystals*; E_a=140± 10 kJ mol^{-1} and ln (A/s^{-1})=40.1±3.7 for *methanol crystals* aged five months. Independently of the history of the material used, these values are very high if compared with those of the inorganic crystal hydrates. This kind of behaviour has already been described [5] and was one of the reasons of the present investigation. It is also to be observed that, even if the thermal curves differ, the kinetic parameters of *aged powder* and *methanol crystals* are similar.

3.1.2. Dynamic runs

In Fig. 2 thermal curves obtained at 2 K min^{-1} of *aged powder* and of freshly prepared *crystals* and *methanol crystals* are compared. A remarkable difference is evident for both the decomposition temperatures (higher for *methanol crystals*) and the shape of the curves (smoother and almost devoid of high temperature spikes for *aged powder*). The long spiky, high temperature tail typical of samples of recrystallized materials indicates that some water vapour remains enclosed in the decomposed product. In Fig. 3, some curves recorded using samples of crystals having approximately the same weight (≈10 mg) but different ageing times are shown. It appears clearly that, on prolonged storage, the curves tend to the temperature range and to the peak shape characteristic of *aged powder*. However, even on very long (two years) ageing, a clear difference remains. For the sake of readability, the curves in Fig. 3 and in the successive Fig. 4 were smoothed twice. The thermal curves indicating the behaviour of *methanol crystals* on ageing are collected in Fig. 4. These curves tended initially to shift towards higher temperatures but, on longer ageing times, such tendencies were reversed.

In spite of the variability in the thermal behaviour of recrystallized materials on ageing, some reproducibility emerges. In fact, two different crystallization batches of *methanol crystals* behaved comparably and,

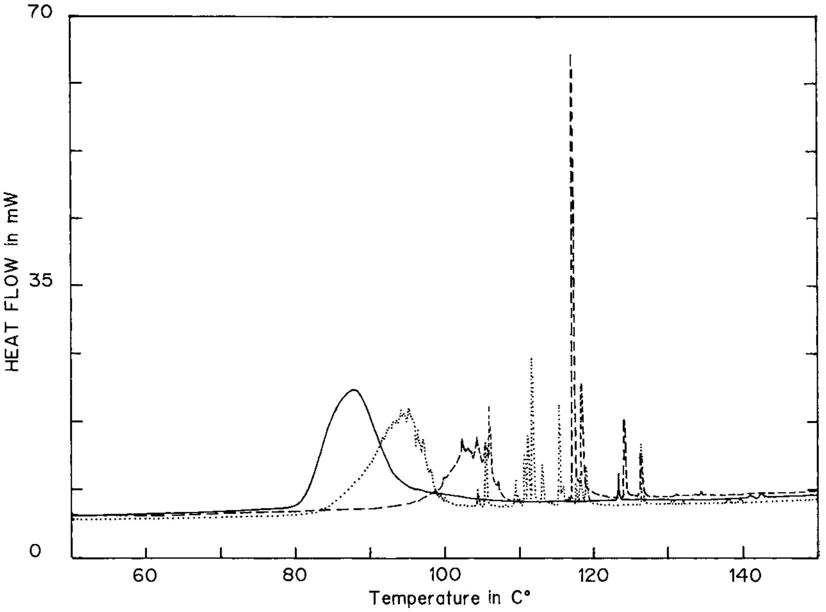

Fig. 2. Comparison of the thermal curves obtained at 2 K min^{-1} of the different LAM preparations: lines as in Fig. 1; 11.3, 11.16 and 6.22 mg, respectively.

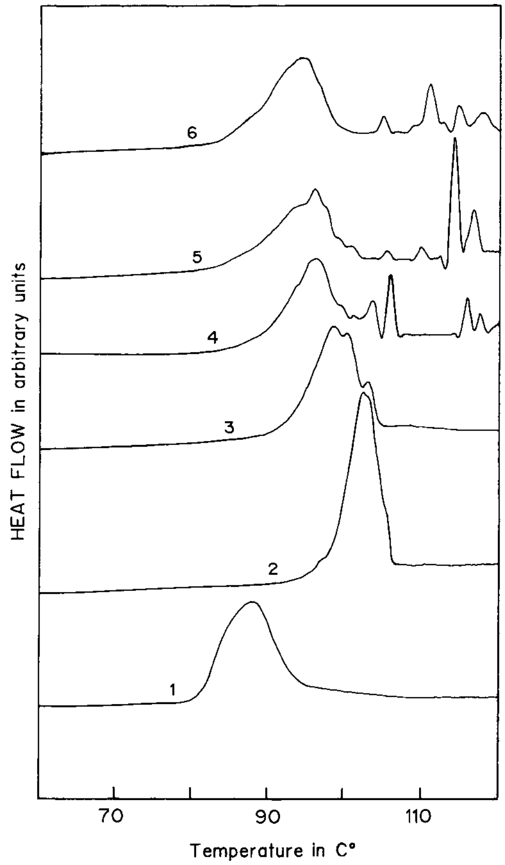

Fig. 3. Thermal curves referring to the ageing of *crystal* samples: curve 1 refers to an *aged powder* sample and is reported for reference; the remaining curves are numbered in order of increasing ageing and the position of the number indicates, approximately, the first deviation from the baseline in the original diagram. The ageing time for curves 2–6 is, respectively, 2, 117, 216, 480 and 816 h.

excluding the spiky region, equivalent samples of the two batches of the same age gave superposable thermal curves.

As a further example of the variability of the thermal responses, Fig. 5 compares the curves obtained at 0.1 K min^{-1}, recorded successively, using a sample of *crystals* (11.93 mg) aged two years, and another one (11.97 mg) of the same batch but kept for 20 h at room temperature in the cell of the DSC under flowing dry nitrogen. Given the sensitivity of our balance (0.01 mg), the latter treatment resulted in no weight loss, indicating that dehydration did not occur.

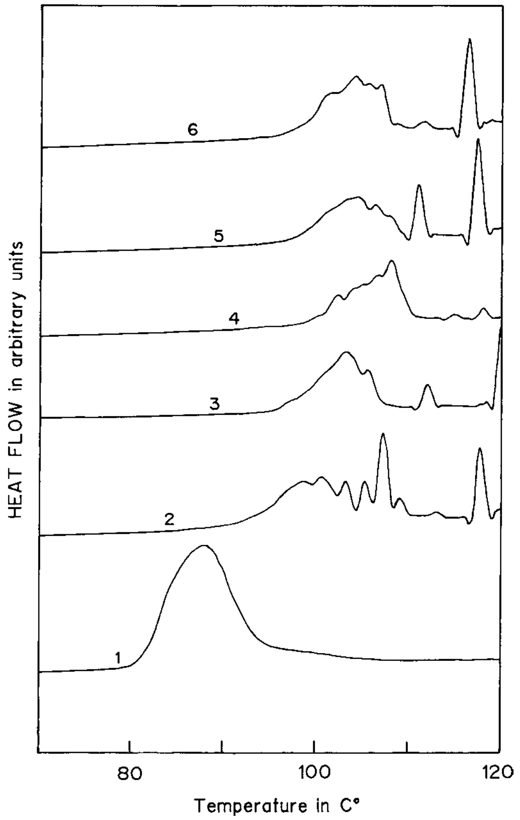

Fig. 4. Thermal curves referring to the ageing of *methanol crystals* samples: for details see Fig. 3, ageing times: 2, 600, 1272, 2040 and 2448 h, respectively.

Conversely, the thermal curves of samples of *aged powder* showed a reasonably good reproducibility with time. As an example, the curves labelled 1 in Figs. 3 and 4 are superposable but were recorded at over six months distance using comparable samples. This is proof of the reliability of the periodically checked instrument calibration and ensures that the differences observed for the recrystallized materials cannot be ascribed to instrument instability. Another indication of instrumental robustness comes from the heats of reaction that, evaluated over the 70–140°C temperature range (i.e. including spikes), those deduced from isothermal runs matched for all materials. Again, the amounts of water lost were always in agreement with the stoichiometry of the following reaction:

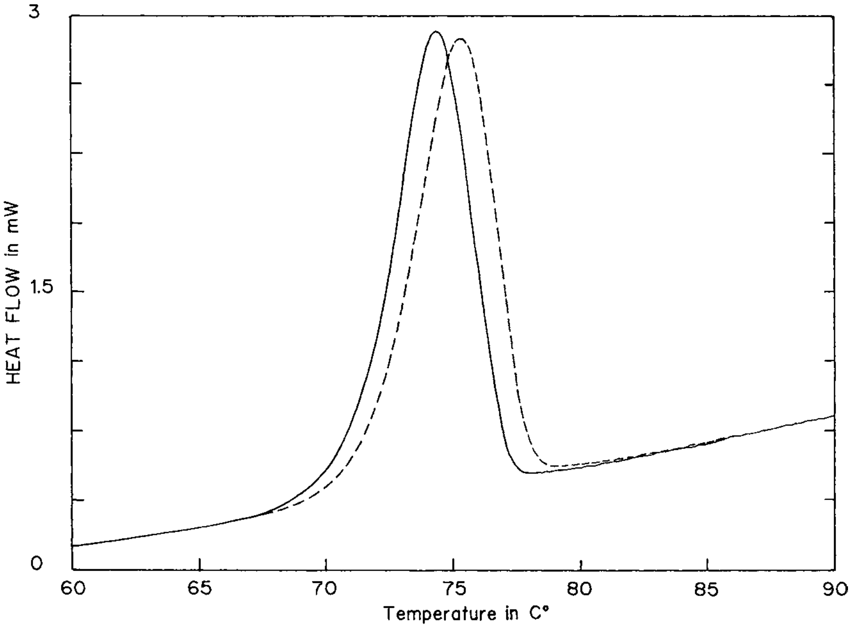

Fig. 5. Thermal curves recorded successively at 0.1 K min^{-1} of two *crystal* samples of almost identical weight, one of which had been kept under flowing dry nitrogen for 20 h at room temperature: solid line 11.93 mg untreated; and broken line 11.97 mg treated.

$$l.\ asparagine \cdot H_2O_{(solid)} \Rightarrow l.\ asparagine_{(solid)} + H_2O_{(gas)}$$

Kinetic analysis of the thermal curves, performed as described in Section 2, indicated for all materials an order-of-reaction type equation with $n=2$ for almost all the experiments, but which tends to $n=1$ for very low heating rates. This agreement with a first-order kinetics parallels that found for isothermal runs at $T\geq70$°C. This means that the mechanism of decomposition depends on both the temperature and heating rate. The kinetic parameters deduced from the curves obtained at 2 K min^{-1} were: E_a=410–550 kJ mol^{-1} and ln (A/s^{-1})=135–180 for *aged powder*; E_a=460–650 kJ mol^{-1} and ln (A/s^{-1})=150–215 for freshly prepared *crystals*. The values of the kinetic parameters for two-year old *crystals* were relatively constant: E_a=545–582 kJ mol^{-1} and ln (A/s^{-1})=172–188; those for freshly methanol crystals were: E_a=570–705 kJ mol^{-1} and ln (A/s^{-1})=180–220 while E_a=490–750 kJ mol^{-1} and ln (A/s^{-1})=150–245 for *methanol crystals* aged five months. We reported ranges of values (rather than average values and errors) for the different preparations, since the kinetic parameters appear remarkably influenced by the above-described variability of behaviour. The very high values of the kinetic parameters, which were over 3.5 times those evaluated from isothermal runs, confirmed that the dehydration of LAM crystals had a remarkable dependence on the presence of a temperature gradient. In addition, at 0.1 K min^{-1}, the kinetic parameters were maximum, thereby confirming that even a small temperature gradient changes the thermal behaviour remarkably. The values of the kinetic parameters decrease from 0.1 K min^{-1} up to 1.5 K min^{-1} and then remain relatively constant up to 16 K min^{-1}. A tentative explanation of this finding is given in Section 4.

3.2. Optical microscopy

Fig. 6 displays a sequence of micrographs recording the behaviour of a LAM single-crystal surface exposing the crystallographic plane *hkl* {011}, heated in the microscope cell at 1.6 K min^{-1}, under flowing dry nitrogen. The overall behaviour is strongly reminiscent of that observed for $Na_2S_2O_3 \cdot 5H_2O$ crystals

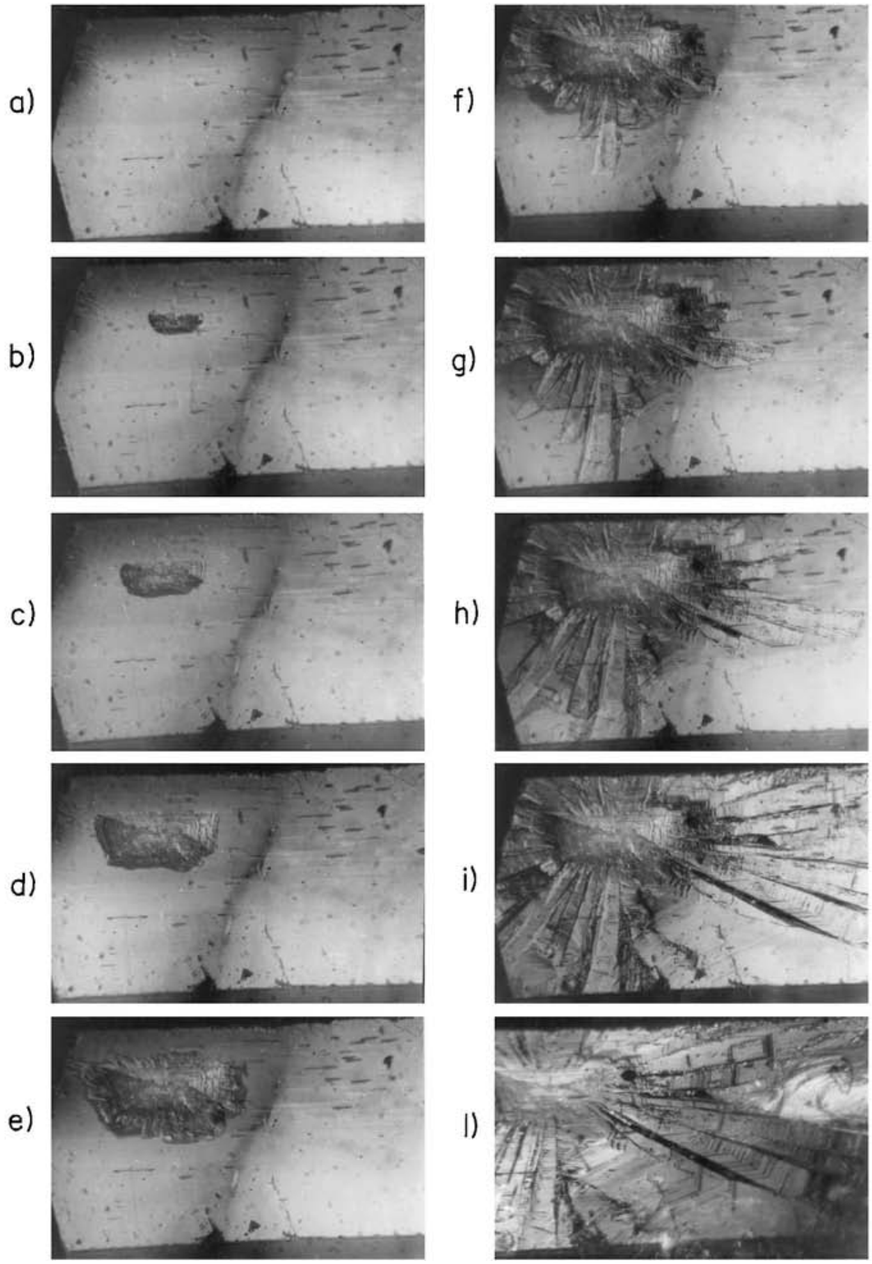

Fig. 6. Sequence of micrographs of the surface of a crystal heated at 1.6 K min^{-1} in the microscope cell: (a) 20°C; (b) 73°C; (c) 75°C; (d) 77°C; (e) 78°C; (f) 79°C; (g) 80°C; (h) 81°C; (i) 83°C; (l) $\sim$50°C, during cooling. Scale bar=100 μm.

and attributed to inner reaction [17]. This remarkable change in texture of the surface results from a dark region which might be a partial detachment of the surface layer from the inner planes of the crystal. In fact, a similar inner dark area is often seen to precede the borders of the ''geometric'' surface corrugation, in the present case seen particularly in Fig. 6(d–f). Another point of interest lies on the right side of

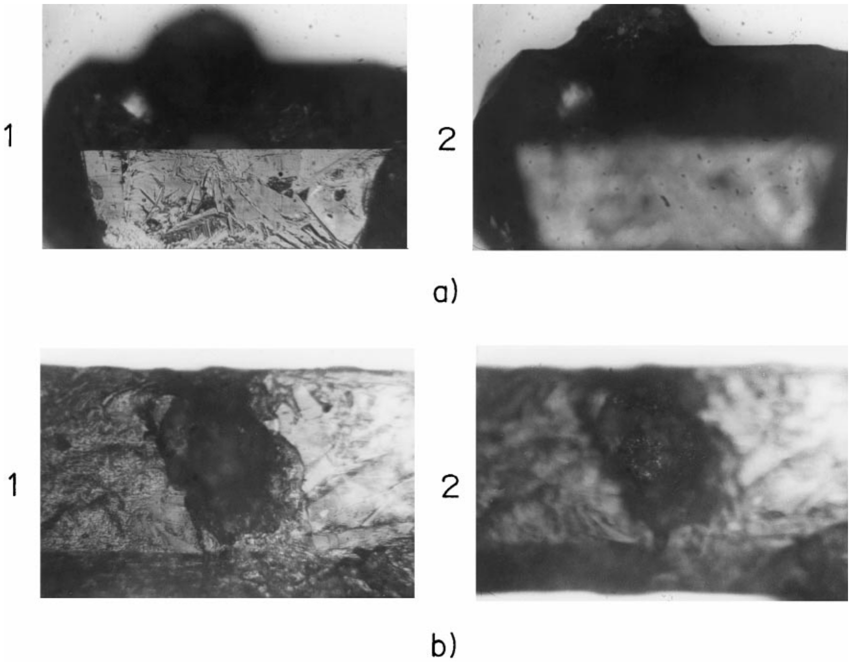

Fig. 7. Swelling of the surface layers to form bubbles: (a) dehydration in the microscope cell (in 1 the crystal surface is focused, while in 2 the bubble is focused); (b) dynamic dehydration in DSC: for 1 and 2, same as above. Scale bar=100 µm.

Fig. 6(l), which was slightly shifted to the left, where a subsurface elliptic whitish area, in which a fluid phase moved in wavelike fashion during cooling, was observed. The presence of fluid phases is also emphasized by the swelling of the surfaces (bubble formation) that can be seen during dehydration in the microscope cell (Fig. 7(a)) or in the residues of the DSC non-isothermal experiments in Fig. 7(b). Indeed the spikes observed in the thermal curves might well be due to sudden deflation of such bubbles. In Fig. 8(a and b) the textures of the surfaces of crystals decomposed in DSC, either isothermally (Fig. 8(a)) or under dynamic conditions (Fig. 8(b)), are compared. The surface in Fig. 8(a) is fine-grained while that of Fig. 8(b) is much rougher, even if it does not reach the roughness of the final frames of Fig. 6. This indicates that the dehydration experiments performed under the microscope (up to ≈120°C max.) are perhaps incomplete and further rearrangement of the surfaces may take place at higher temperatures. The different final textures of the surfaces resulting from isothermal or dynamic runs may be the result of the different transformation mechanisms evidenced also by the kinetics of the thermal curves. No remarkable differences in the behaviour of *crystals* and

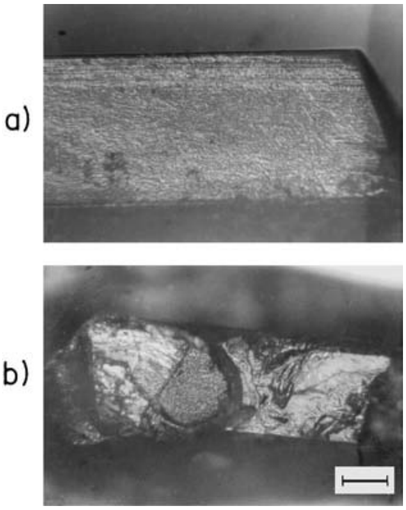

Fig. 8. Comparison of the surface damages deriving from (a) isothermal and (b) dynamic dehydrations. Scale bar=100 µm.

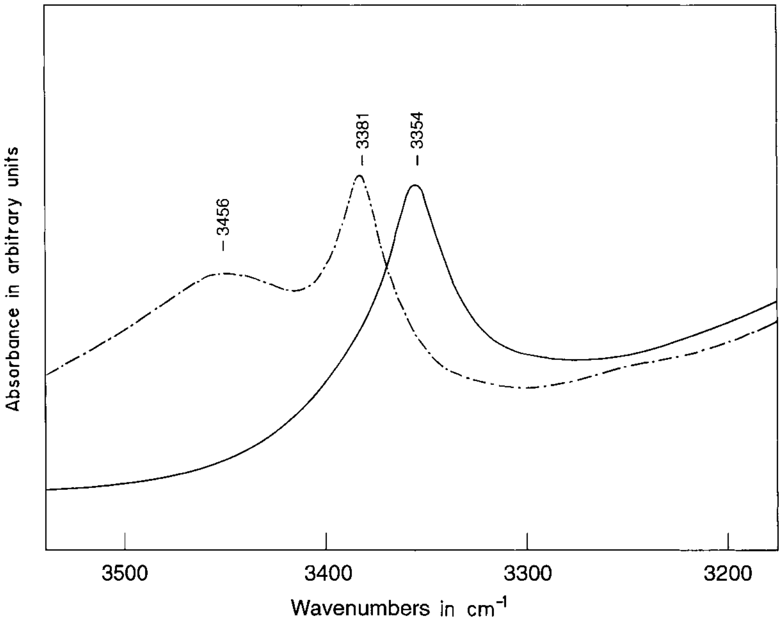

Fig. 9. FT-IR spectra of untreated *aged powder*-type LAM and of a fully dehydrated sample.

methanol crystals were displayed during optical microscopy.

3.3. FT-IR techniques

In Fig. 9, the 3200–3500 cm^{-1} spectra of *aged powder* (broken line) and of a fully dehydrated sample (solid line) after grinding and pelletization with KBr are compared. It is evident that, on dehydration, the 3456 cm^{-1} band attributed to –OH stretching of water disappears while the 3381 cm^{-1} band attributed to –NH stretching shifts to 3354 cm^{-1}. The same happens in Fig. 10, where the microreflectance spectra of a 50×150 μm portion of a single-*crystal* surface exposing the crystallographic plane *hkl* {011}, recorded at 1 K min^{-1} from 30° up to 70°C, are displayed. Beyond confirming the previous findings related to the bulk system, these spectra indicate that the surface layer of the crystal (a few μm thick), from which the spectral response originates, starts to lose water at ≈55°C and is fully dehydrated at the relatively low temperature of ≈70°C. This takes place without apparent changes in the surface texture apart from the appearance of a small (≈10 μm^2) dark spot, similar to that in the initial frames of Fig. 6.

4. Discussion

The remarkable variability of thermal dehydration of recrystallized samples of LAM is the striking feature of the present research. We have already reported on modifications of the thermal behaviour of some compounds [3–5,18] attributed to subtle changes of the crystal surfaces caused by different crystallization procedures, by ageing or by mechanical treatment in selected atmospheres. The multiplicity of behaviour seen in this study has not been previously observed. However, in the present instance, this lack of reproducibility is the main finding. Indeed the sensitivity of the apparatus, the evidences of reproducibility and the proven reliability of the data treatment ensure that the experimental results faithfully represent the behaviour of LAM crystals on heating. In other words, the observed variability is real and representative of a system whose decomposition is dominated by the behaviour of the outer surfaces which, in turn and unless aged for very long time (*aged powder*), yield to even subtle changes in storage and experimental conditions.

On the grounds of previous studies [1–5], the behaviour of *crystal* samples in dynamic thermal runs

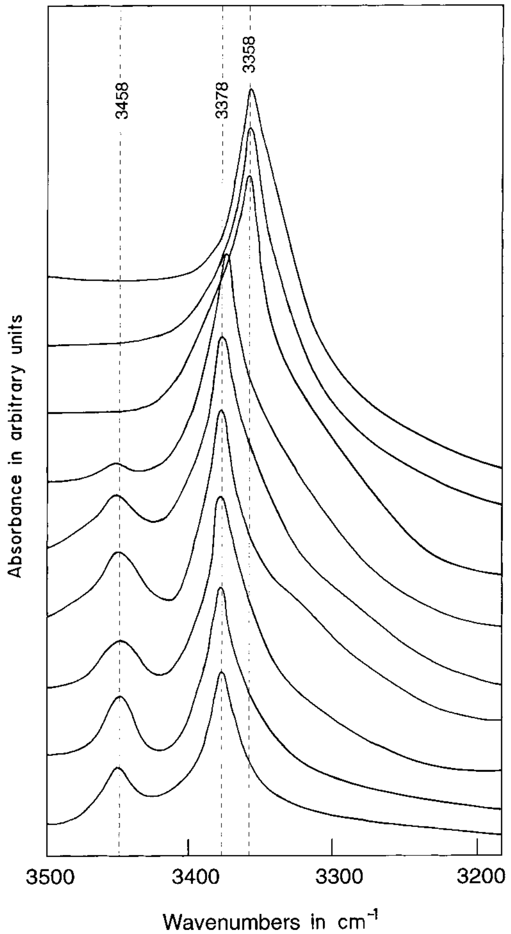

Fig. 10. FT-IR microreflectance spectra of a single crystal heated at 1 K min^{-1}: from bottom to top the spectra were recorded at temperatures of 23°C; 30°C; 40°C; 50°C; 61°C; 70°C; 72.5°C; 73°C; and 74°C.

on ageing was expected. Indeed the progressive regression of the thermal curves along the temperature scale (i.e. towards the position taken by the prolonged aged *crystal* samples) can be attributed to an increasing deterioration of the perfection of the crystal surfaces. This would be caused by reciprocal scratching due, e.g. to the manipulations necessary to withdraw samples for analysis. The ageing behaviour of *methanol crystal* samples requires some further consideration. The initial shift of the thermal curves towards higher temperatures may be attributed to the progressive desorption from the surfaces of the methanol used as the habit-modifying solvent in the crystallization solutions, which can lead to reconstruction [19] of the exposed surfaces. On further ageing, the direction of the shift reverses and parallels that of *crystal* samples. The fact that, on the whole, the curves of *methanol crystal* samples are usually in temperature ranges somewhat higher than those of *crystal* samples is again attributed to reconstruction that generates fresh surfaces. Hence, the difference in behaviour between *crystal* and *methanol crystal* samples may be ascribed to surface reconstruction that may show alternative behaviour on different exposed planes.

Another proof of the importance of the state of the surface is the shift (Fig. 5) caused by a 20 h residence of the sample, with no apparent changes, under flowing dry nitrogen. It seems that such a treatment caused some modification of the surfaces, generating an impermeable film that slows down further dehydration. The presence of such a film is also supported by the spiky shape of high-temperature portion of the dynamic thermal curves, attributed to sudden releases of the gaseous product of the inner reaction.

Concerning the kinetic parameters derived from the dynamic conditions, the *methanol crystal* material for both, fresh and aged samples, shows the highest values. Methanol desorption and surface reconstruction can again be considered responsible for this finding as the rate of such processes is reputed to increase rapidly with temperature. This agrees with the fact that fresh *methanol crystal* samples show the highest average value of the activation energies and frequency factors.

Coming to isothermal runs, the dehydration of *aged powder* samples in flowing dry nitrogen was completed at measurable rate, even at 55°C, while somewhat higher temperatures (>60°C) were required for *crystal* and *methanol crystal* samples. In agreement with TSM, such diversity is probably due to the different permeabilities of the initially dehydrated surface layers caused by the evident disparities of surface defectivity. In fact, the experimental results (particularly microreflectance FT-IR) prove that, at least at the beginning of the runs, water was removed from the outer layers of the crystals. In the present case, an outer dehydrated layer as a sort of polymeric film may be perceived as enveloping the whole crystal and preventing the escape of the water vapour generated by an inner reaction. In such situations, it is known that water vapour is highly hindered with a consequent increase of the activation energy [20].

According to Bawn [21], the decomposition of organic solids does not entail the formation of ''nuclei''. This seems to be confirmed in the present study by optical microscopy experiments which evidenced neither ''nuclei'' nor crystallization. Hence, no discontinuities of the reacted surface layer were generated by crystallization. This is particularly important in the case of recrystallized reactants whose surfaces, containing a limited amount of visible imperfections, are apt to generate continuous dehydrated films which are impermeable to the gaseous reaction product. This may account for the high activation energies observed in the present case. In terms of TSM, this implies an extremely slow third stage (the crystallization of the product of the reaction) and entails also a rather difficult second (diffusional) stage. There is probably enough time for purely diffusional escape of the gaseous reaction product through the surface layer only in isothermal runs at low or medium temperatures. This also explains the relative uniformity of reacted crystal surfaces in comparison with those of the crystals that underwent dynamic decomposition (Fig. 9) and indicates, again, the importance of the presence of a temperature gradient. In the latter case, the presence of high inner pressures and liquid phases induces relevant deformations of the surface layer eventually leading to bubble formation.

The kinetic aspects of the dehydration of LAM require, however, some further considerations. An important point is that in isothermal runs, apart from temperatures $\geq 70^\circ$C, the reaction shows strict obedience to a $n=3$ Avrami–Erofeev equation. It is known that this requires random nucleation and appears to be in contrast to that described by Bawn [21], unless submicroscopic ''nuclei'' are envisaged. On the other hand, this kind of isothermal obedience was also found for other inorganic systems and it is quite common [14]. Thus, when an inner reaction is possible, the Avrami–Erofeev model is a rather general way of describing decompositions. To clarify our point of view let us envisage a crystal as a ''dynamic'' entity where the ''positions'' of the lattice constituents (as evaluated e.g. by X-ray diffraction) are only the loci of highest occupational probability. The ''motions'' of a single lattice constituent are the result and contribute to the ''motions'' of the other constituents (cooperativity). In the bulk the situation can be considered ''quasi static'' and the spatial distribution almost regular but at surfaces this regularity breaks down because lattice constituents lack partners on one side and this may make easier the release of some lattice constituents (e.g. water in crystal-hydrates) to the superposed gaseous phase. However the above written is not the only way to start a transformation: lattice defects and ''motions'' fluctuations may well generate inner reaction sites (nuclei?) that may result randomly distributed particularly in the case of fluctuations. This second possibility not only accounts for internal reaction and for the observed Avrami-Erofeev kinetic obedience, but can also explain the observed independence of (or very poor dependence on) structure of the reaction [1–5]. Indeed, ''motions'' cooperativity entails that reaction sites ''deform'' their surroundings... etc., so that further reaction takes place in a continuously changing environment (reaction front). Systems of this kind should not result particularly sensitive to ''geometric'' dependencies like preferred lattice planes or directions. This point is particularly interesting and is supported both by the required randomness and by the observed increase of inner pressure caused by the formation of impermeable films on ''all'' crystal surfaces independently of their orientation. The above does by no means entails also product crystallization is independent of structure. These considerations have been developed to understand the behavior of the present system but are believed to be of general applicability; in particular the fact that the reaction appears to be independent of structure seems typical of all decompositions interpretable in terms of our TSM [1].

A last consideration concerns the very high kinetic parameters found in dynamic runs, that must be an effect of the presence of a temperature gradient. As the kinetic parameters have the maximum at 0.1 K $\min^{-1}$ and they decrease on increasing the heating rate, a low temperature gradient must be the critical factor driving this behaviour. By analogy with recent findings [22,23], it is possible that in the low temperature gradient runs, the surface has sufficient time to yield to the structural changes connected with the increase in temperature. Hence, the layer formed becomes more impermeable than at higher heating rates. Increasing the heating rate also produces a change in the mechanism, namely that from first- to second-order reaction. Similar occurrences have been observed [1,2] and explanations in terms of increase of the inner pressure with temperature have been given [1], that may apply also to the present decomposition. Second-order kinetic dependence may also be the result of the reaction taking place homogeneously in the liquid phase whose presence was ascertained by optical microscopy. Such kind of reaction would probably be enhanced by increase in temperature. This might well supply another plausible interpretation of the high activation energies deduced from the dynamic runs.

5. Conclusions

The dehydration of LAM crystals is a complex process showing remarkable variability. The transformation can be affected by crystallization modalities, by ageing and by storage and experimental conditions, in other words by all those parameters that can affect the nature and properties of the crystal surfaces. All the abovesaid makes this system interpretable in terms of our TSM.

Considering that the system is characterized by

(i) relevant sensitivity to the state of the crystal surfaces,
(ii) the initial presence of a dehydrated surface layer, and
(iii) an inner reactivity

we conclude that our three-stage mechanism (TSM) may also account for the experimental results in the present case.

We believe that studies of this kind will be of great interest to those concerned with the storage of perishable materials (e.g. high-priced pharmaceuticals). In fact, an accurate treatment of the outer surfaces of such materials may prove invaluable for this purpose.

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