Journal of Thermal Analysis, Vol. 34 (1988) 487–495

HEATING RATE AND THE DEHYDRATION OF $\alpha \cdot NiSO_4 \cdot 6H_2O$ SINGLE CRYSTALS

G. G. T. Guarini and *M. Rustici*

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORENCE,
VIA GINO CAPPONI, 9–50121 FIRENZE, ITALY

Dehydrations of $\alpha \cdot NiSO_4 \cdot 6H_2O$ single crystals cleaved parallel to (001) have been performed both at constant and linearly increasing temperature. The thermal curves recorded are found to change remarkably in shape by changing the rate of temperature increase (scan speed). A number of unforeseen events, like fluid formation and bubble swelling, taking place in the crystal under investigation were visually observed and photographically recorded by coupling a Wild microscope to a Perkin-Elmer DSC-1b apparatus. An interpretative hypothesis is proposed based on the initial formation of a dehydrated layer on the crystal surfaces. The properties (perfection, continuity and permeability to the gaseous product) of such a layer are one of the parameters governing the evolution of the system. Other parameters are the rate of product crystallization, the rate of inner gaseous product generation and their variations with temperature.

One of the advantages of thermal methods in the study of chemical change comes from the ease with which, at least in principle, the deduction of kinetic parameters is possible. Consequently many methods of data treatment have been theoretically and empirically devised and tested [1]. Among these the ones based on the use of different heating rates are here considered even if indirectly. In effect the latter methods are based on the assumption that changing the heating rate does not change the mechanism. Evidence will be given here that the dehydration of $\alpha \cdot NiSO_4 \cdot 6H_2O$ single crystals [2–4] is one of the cases in which the above assumption is invalid. Indeed the behaviour of these crystals changes dramatically with the rate of temperature increase. As for many other aspects the dehydration of the same compound closely resembles that of other salt hydrates, it descends that for these reactions great care is necessary to select the right treatment of thermal data.

Correspondence to: Prof. G. G. T. Guarini.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Large single crystals of $\alpha \cdot NiSO_4 \cdot 6H_2O$ of good perfection were obtained by slow evaporation of solutions of Merck "pro analysi" material in doubly distilled water additionated of some sulphuric acid. The flatness of the (00l) cleavage faces ensured good thermal contact with the bottom of the aluminium sample pans of both the Mettler TA 2000 thermal analyzer and the Perkin–Elmer DSC–1b differential scanning calorimeter. Isothermal (60–70°) and variable temperature runs were performed in a flow of dry nitrogen of 13 to 16 $cm^3 \cdot min^{-1}$. The crystals allowed to decompose in the Perkin–Elmer apparatus were observed and photographed by means of a Wild microscope, equipped with an Olympus OM2 camera, working through the glass window of the sample holder cover. Illumination was ensured by a Volpi Intralux twin optical fiber illuminator shining equally light on sample and reference holders. Dehydrations and rehydrations of cleaved crystals of nickel sulphate hexahydrate under comparable conditions were studied also by optical microscopy employing the reflection mode of a Reichert Zetopan microscope equipped with interference contrast. In this case the dehydration was sometimes performed by vacuum (ca. 10^{-2} Pa).

Results and discussion

Optical microscopy evidenced that partially dehydrated (001) cleavage faces of the crystals studied underwent, upon rehydration, the typical retexturing known as "orange peel" [5, 6] confirming that also in this case the initial dehydration extended to the whole surface. Under this aspect, $\alpha \cdot NiSO_4 \cdot 6H_2O$ showed the same behaviour as other salt hydrates investigated in precedence. Also, under prolonged dehydration, the usual "nuclei" appeared on the observed surfaces and subsequently grew to cover the whole surface of dehydration product.

According to the above findings the thermal behaviour of the crystals should have been characterized by a single isothermal dehydration endotherm. Also a double (surface + bulk) rehydration exotherm like the one in Fig. 1a was expected [7]. However, in the experimental conditions employed, the isothermal dehydrations performed in the Mettler apparatus were found to give endotherms splitted into two separated portions (Fig. 1b) again attributed to surface and bulk processes by analogy both with the partial separation already observed in the dehydration of $Na_2S_2O_3 \cdot 5H_2O$ [8] and with the complete one evidenced in the reaction of chrome alum surfaces with ammonia gas [9].

The isothermal dehydration ended after a weight loss corresponding to the elimination of two of the six water molecules in the lower part of the temperature

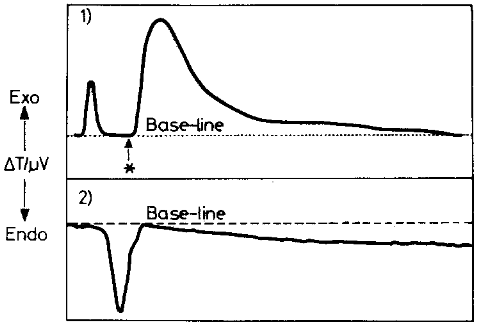

Fig. 1 1) Typical thermal curve recorded during the isothermal rehydration of dehydrated crystals [6; 7]; 2) typical thermal curve recorded during the isothermal ($T = 65°$) dehydration of a cleaved crystal of the title compound by a flow of dry nitrogen. The drawing shows only the initial 90 min of the dehydration which lasts for ca. 12 hours

range investigated and after a somewhat higher loss in the upper part. On the contrary the end product in the increasing temperature runs was invariably $NiSO_4 \cdot H_2O$ [2]. In effect up to 250° the percent weight loss and the total heat of transformation were found independent of the heating rate (scan speed, (SS) in deg/min) being respectively 34.2% and 266 ± 14 kJ/mol (i.e. 53.3 ± 3 kJ/mol H_2O [7]).

The change in shape of the thermal curves with scan speed (SS) is illustrated in Fig. 2. It is evident that at $SS \leqslant 2$—apart from the small initial endotherm, evident in the $SS = 0.1$ curve, and attributed to surface dehydration—the thermal curve is unique. On the contrary at $SS \geqslant 2$ the process tends to split into two endotherms corresponding approximately to the elimination of 3 and 2 water molecules respectively. At $SS = 4$ between the two main endotherms there is a zone of "ups and downs" changing from crystal to crystal but generally comprised in the 125–145° temperature range. At even higher SS the themal curve increases in complexity tending to resemble (were the shoulders resolved) the one reported in Ref. 2. The initial endotherm is found to decrease in favour of a central one which could not be ascribed to some phase transition because of the constancy of the overall heat change.

To gain further information the experiments by the Perkin–Elmer apparatus allowing inspection of the sample were started. Making allowance for the change due to the differences between a heat flow and a power compensated apparatus, the newly recorded thermal curves corresponded to those shown in Fig. 2.

Visual inspection revealed an unexpected sequence of events somewhat differentiated depending on the perfection of the observed cleavage surfaces.

For surfaces of good perfection:

i) at $SS \leqslant 2$ the usual behaviour is observed and the crystallization of the

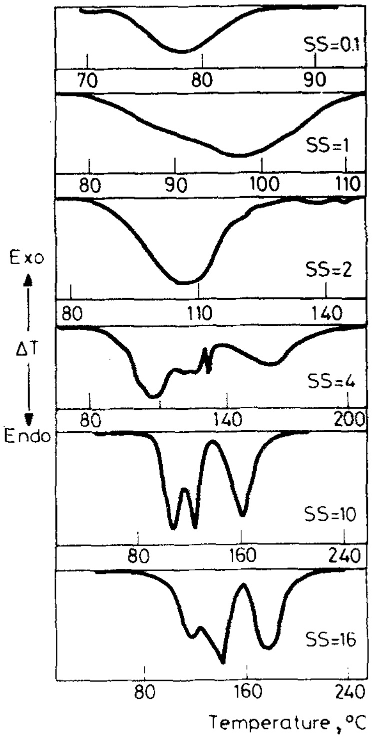

Fig. 2 Thermal curves of the dehydration to monohydrate of cleaved single crystals of the title compound recorded at various scan speeds

dehydrated product starts at localized positions to spread successively over the whole surface (Fig. 3a, b, c). The smoothness of the thermal curve indicates that subsequent water loss must take place evenly through the microcrystalline product layer covering the surface. Kinetic analysis of the curves could be performed and the agreement with the findings in Ref. 2 was particularly good for the lowest values of the scan speed.

ii) at SS = 4 the spreading of product crystallization through the surface does not reach the completeness and fluidification of the unaltered portions takes place followed by the swelling of the surface itself to form bubbles (Fig. 4a, b, c). This phenomenon is the responsible of the thermal behaviour in the 125–145° range. It is also thought that fluidification may account for the conductivity data reported in Ref. 3.

iii) at SS > 4 fluidification (and at SS = 16 even crystallization of the product) is often preceded by the collapse of the lattice as shown by sudden crack formation (Fig. 5a, b, c). This phenomenon is reputed the cause of the blurring of synchrotron

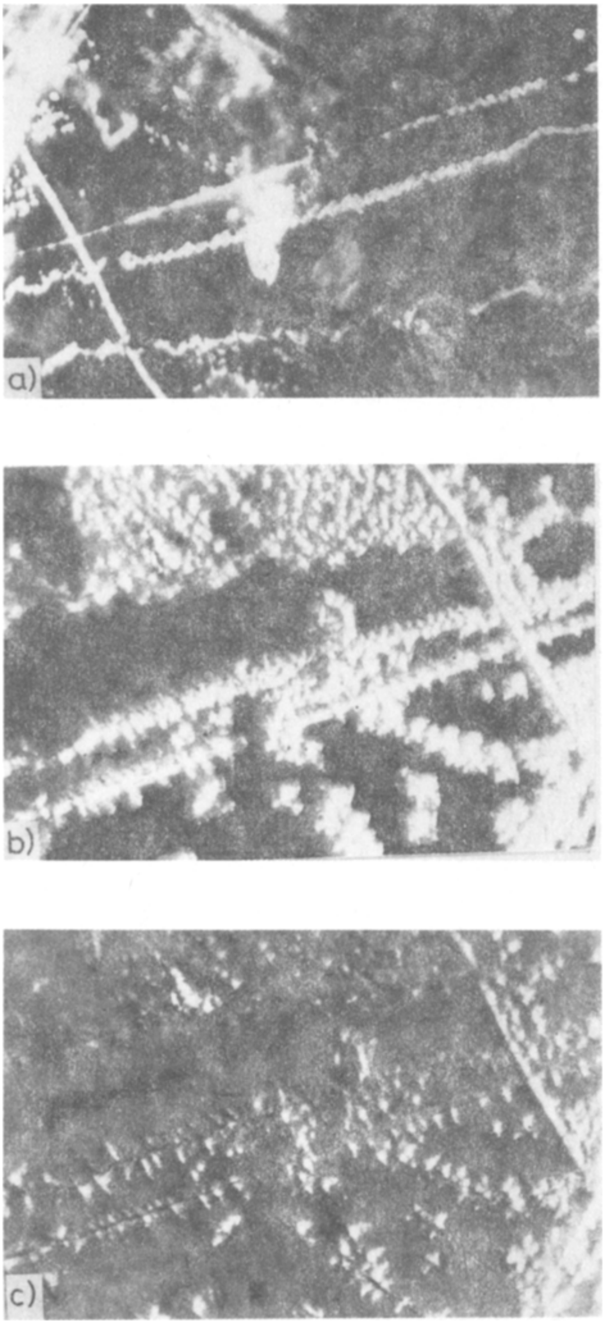

Fig. 3 Sequence of photographs recorded during one of the experiments at SS = 2. The crystallization of the product has enough time to spread over the whole crystal surface. (Magn. x20)

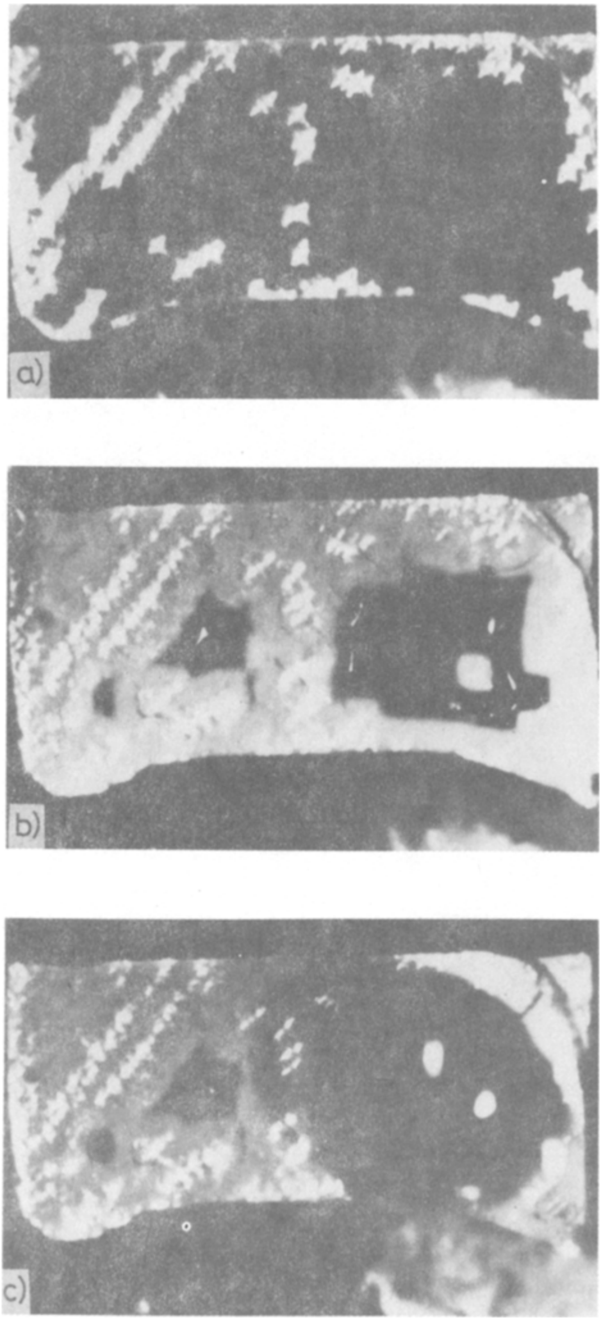

Fig. 4 Sequence of photographs recorded during one of the experiments at SS = 4. Crystallization of the product, even if initiated at defect sites, does not succeed in spreading over the whole surface and liquefaction (Fig. 4b) takes place eventually followed by bubble formation (Fig. 4c). (Magn. x15)

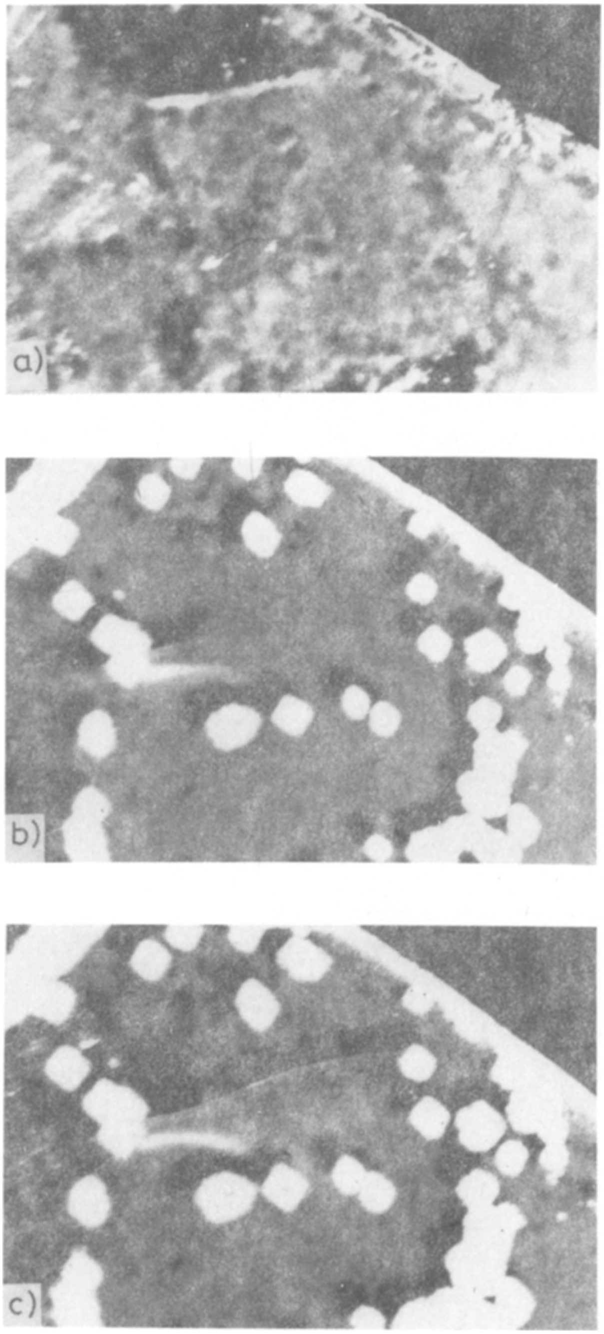

Fig. 5 Sequence of photographs recorded during one of the experiments at SS = 16. Again some crystallization takes place at defective positions but collapse of the lattice (cracking) precedes liquefaction and bubble formation. (Magn. x20)

radiation topographs reported in Ref. 4. Successively product crystallization takes place on the defects introduced by cracking.

If the crystal surfaces are characterized by a relevant number of imperfections like steps etc. the above reported phenomenology becomes less pronounced and tends to be displaced towards the higher scan speeds. This finding is confirmed by experiments on crystals whose surfaces had previously been scratched to introduce an enormous number of surface defects. In this case the crystallized product immediately covers the surface while the corresponding thermal curve tends to an unification of all the observed endotherms and becomes almost independent of the scan speed. Furthermore, at variance with Ref. 2, experiments with ground powders always gave a single broad endotherm.

All the above phenomena can be understood if it is admitted that (as supported by the "orange peel" formation and by the double isothermal endotherm) at the very beginning of the transformation a dehydrated layer is formed on the whole surface of the crystal [10]. Then it is easy to believe that what happens is due to an interplay among: a) the rate of water formation and its change with the temperature; b) the perfection of the surface layer and its permeability to the gaseous product (both changed by product crystallization); c) the rate of crystalline product formation and its variation with temperature.

Again the importance of defects in the reactivity of solids is stressed even if their role appears to be that of sites of easy product crystallization rather than that of sites of enhanced reactivity [11]. Indeed it is believed that the crystallization of the product, favoured by an high defect density, alters the continuity (and therefore the permeability) of the initially formed surface layer thus modifying the pressure of the gaseous product inside the crystal and consequently the evolution of the system as a whole.

Further details and considerations can be found in a preliminary note already appeared [12], anyway the above results are thought to be of strong support to the warning against an indiscriminate use of the thermal methods to get kinetic parameters [13].

References

1 M. E. Brown, D. Dollimore and A. K. Galwey in "Comprehensive Chemical Kinetics", C. H. Bamford and C. F. H. Tipper Eds., Vol. 22, Elsevier, Amsterdam, 1980.

2 J. M. Thomas and G. D. Renshaw, J. Chem. Soc., A (1969) 2749–2759.

3 D. M. Minic, M. V. Susic, U. B. Mioc and N. A. Petranovic, Materials Chemistry and Physics, 12 (1985) 389.

4 D. B. Sheen and J. N. Sherwood, Materials Science Monographs, 28A (1985) 93.

5 A. K. Galwey, R. Spinicci and G. G. T. Guarini, Proc. Roy, Soc., A378 (1981) 477.

6 G. G. T. Guarini and L. Dei, J. Chem. Soc. Faraday I, 79 (1983) 1599.

7 L. Dei, G. G. T. Guarini and S. Piccini, J. Thermal Anal. 29 (1984) 755.
8 G. G. T. Guarini and S. Piccini, Proceedings of the 6th AICAT Meeting, Naples, 1984, C8.
9 A. K. Galwey and G. G. T. Guarini, Reactivity of Solids, 1 (1986) 207.
10 L. Dei, G. G. T. Guarini and S. Piccini, Materials Science Monographs, 28B (1985) 691.
11 J. M. Thomas, Advances in Catalysis, 19 (1969) 293.
12 G. G. T. Guarini and M. Rustici, Reactivity of Solids, 2 (1987) 381.
13 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, J. Thermal Anal. 29 (1984) 775.

Zusammenfassung — Parallel zu (001) gespaltene α-$NiSO_4.6H_2O$-Einkristalle wurden bei konstanter und linear ansteigender Temperatur dehydratisiert. Die registrierten thermischen Kurven veränderten ihre Gestalt mit der Aufheizgeschwindigkeit beträchtlich. Eine Anzahl von unvorgesehenen Vorgängen, wie Flüssigkeitsbildung und Blasenbildung im Kristall, wurden visuell beobachtet und photographisch durch Verbindung eines Wild-Mikroskops mit einer DSC-1b-Apparatur von Perkin-Elmer aufgezeichnet. Eine auf der Bildung einer dehydratisierten Schicht auf der Kristalloberfläche basierende Hypothese wird zur Interpretation vorgeschlagen. Die Eigenschaften (Vollkommenheit, Kontinuität und Permeabilität für gasförmige Produkte) einer solcher Schicht sind einer der die Dehydratisierung des Systems bestimmenden Parameter. Andere Parameter sind die Kristallisationsgeschwindigkeit des Produktes, die Geschwindigkeit der intrakristallinen Bildung des gasförmigen Produkts sowie deren Änderung mit der Temperatur.

Резюме — При постоянном и линейном нагреве изучена дегидратация монокристаллов α-$NiSO_4.6H_2O$, расщепленных вдоль плоскости (001). Вид термических кривых заметно изменяется с изменением скорости нагрева. Ряд таких непредвиденных явлений, как образование псевдожидкости и пузырьковое набухание, имеющих место в процессе исследования кристаллов, визуально наблюдали и были сфотографированы путем сочленения дифференциального сканирующего калориметра фирмы Перкин-Эльмер с микроскопом Вильда. Высказана гипотеза о первоначальном образовании дегидратированного слоя на поверхностях кристалла. Такие свойства слоя, как совершенство, непрерывность к проницаемость к газообразному продукту, являются одними из параметров, контролирующих оценку системы. Другими параметрами являются скорость кристаллизации продукта, скорость образования внутреннего газообразного продукта и их изменения с температурой.