KINETICS OF THERMAL DEHYDRATION OF $Ba(ClO_3)_2 \cdot H_2O$

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The kinetics of thermal dehydration of microcrystalline powders and single-crystals of barium chlorate monohydrate were studied by differential scanning calorimetry. The computer elaboration of thermal data showed that a single kinetic law could not account for the whole decomposition; moreover, different laws had to be used for powders than for single-crystals, whose reaction appeared diffusion-limited towards the end of the dehydration. Optical microscopy was extensively used as an independent source of information to clarify some of the thermal results and to gain a deeper insigth into the possible reaction mechanism.

The use of thermal methods to study the reactivities of solids has become more and more popular because of the relatively easy experimentation. Parallel to this growth, a deep improvement of the underlying theory has taken place [1]. However, the deduction of meaningful kinetic parameters is not always as straightforward as it might appear and a careful analysis of the thermal data, usually performed by computer techniques, is necessary. Nevertheless, this is sometimes not enough and an independent source of information is required.

Optical microscopy is particularly useful when reactions of the type $A_{solid} \rightarrow B_{solid} + C_{gas}$, in which nucleation takes place on external surfaces, are considered; in fact, nucleation and growth rates are easily obtained. Moreover, if correspondence of nuclei and sites of emergence of dislocations is evidenced, some insight into the reaction mechanism may be gained by a determination of the possible dislocation systems in the parent crystal, using the etching technique.

In a study on the kinetics of thermal dehydration of a number of crystal hydrates and hydroxides, planned to compare structure, defects and reactivity in order to seek possible correlations, barium chlorate monohydrate (BCM) was taken into consideration because a) its structure is known; b) crystalline powders and single-crystals are easily obtained; c) the water molecule is lost stoichiometrically in a single step; d) its crystals are easily cleaved.

Moreover, preliminary thermal runs had evidenced some discrepancies in the behaviour of powders and single-crystals which were not amenable to the effects of the parameters which usually influence the thermal curves (e.g. sample mass, nitrogen flow, scan speed) [2]. BCM therefore appeared particularly suitable to check the complementarity of thermal methods and optical microscopy.

In the present paper we report on the kinetics of thermal dehydration of BCM on the basis of thermal and microscopic evidence. The temperature coefficients of the rate constants of the laws found applicable in the different ranges of fractional decomposition (α) are given in the Arrhenius form to make them more easily comparable with the corresponding data in the literature. A word of warning is necessary at this point: as customary, all the deductions in this paper are based on the validity of the Arrhenius equation. There is, however, some evidence [3] that activation energies (E_a) and frequency factors (A) may show some shortcomings when they refer to the reactivity of solids.

Experimental

Riedel de Haen BCM was recrystallized from bidistilled water. Two slightly different procedures were used to prepare the powder samples: *type A* microcrystals were obtained by slowly cooling to room temperature a solution saturated at $60-70°$; *type B* microcrystals were prepared by slowly cooling to room temperature part of the same saturated solution maintained under continuous magnetic stirring (Fig. 1). Single-crystals were prepared by slow room temperature evaporation of a saturated solution; their morphology was almost exactly that reported by Groth [4]. The interfacial angles, measured by optical goniometry, were in good agreement with those reported [4] and with those computed according to the structure refinement by Sikka et al. [5]. Once dried, the microcrystals were sieved to collect fractions having almost the same size. No differences were evidenced in the dehydration of samples of the same type but of different mean size.

A Perkin—Elmer DSC-1b differential scanning calorimeter was used to obtain the dehydration thermal curves to be used for the determination of kinetic parameters. Unfortunately, the temperature at which the reaction started (ca. 90°) was too high to allow a recording of reliable isothermal runs, owing to the time necessary to balance the calorimeter at the maximum sensitivity. A set of runs was devised for both powders to provide evidence of possible effects of sample weight (6, 8, 10 mg), nitrogen flow (0, 5, 10, 15, 20, 25, 30 ml/min) and scan speed (0.5, 1, 4, 8°/min). As regards single-crystals, the mass was maintained as constant as possible (ca. 20 mg), while the nitrogen flow and the scan speed were varied as previously described.

A thin layer of graphite was used in both the sample and the reference pans to match the thermal emissivity [6]. The single-crystals were embedded in graphite powder to ensure a reasonably good thermal contact. The water loss, determined by weighing the samples before and after the runs, was almost stoichiometric.

To obtain the kinetic parameters, the peak heights were measured at regular temperature intervals, and the peak areas as well as particular functions of α were obtained by means of a CII 10070 computer.

The nucleation and growth processes on as-grown and cleavage faces of single-crystals were studied in air at constant and variable temperature by means of

Fig. 1. BCM microcrystalline powders: a) *A* type; b) *B* type. (Magn. ×90)

a Reichert Zetopan microscope equipped with hot-stage, interference contrast and interferometer after Nomarski [7] and an Exacta WX 1000 camera.

Results

1. *Calorimetric measurements*

The measurement of peak areas gave the following values for the heat of dehydration of BCM:

powders (both *A* and *B* types) 13.6 ± 1.0 kcal/mole
single-crystals   12.8 ± 1.5 kcal/mole

The kinetic analysis of the thermal curves was performed as reported in previous papers [8, 9]. From an examination of the Arrhenius plots of a number of laws usually applied to the kinetics of decomposition of solids [10], some evidence emerged:

i) in no run could a single kinetic law account for the whole decomposition;

ii) excluding the initial portions of the reaction, the laws which account for the decomposition of powders are not applicable as such to the decomposition of single-crystals;

Table 1

Summary of the kinetic parmeters deduced from the thermal curves

Kinetic laws	Rate equations	Range of validity		E_a	log A
		Powders			
Power law $(n = 2)$	$\dfrac{d\alpha}{dt} = k \cdot \alpha^{1/2}$	$\alpha < 0.07$ A type $\alpha < 0.15$ B type		23.2 ± 2.5 22.5 ± 1.9	10.11 ± 1.1 9.88 ± 0.8
Avrami-Erofeev law $(n = 2)$	$\dfrac{d\alpha}{dt} = k \cdot (1 - \alpha) \cdot$ $[-\ln(1-\alpha)]^{1/2}$	$0.20 < \alpha < 0.50$ A type $0.25 < \alpha < 0.65$ B type		$19.5(*)$ 37.8 ± 3.1	$5.30\,(*)$ 15.8 ± 3.1
Decay law	$\dfrac{d\alpha}{dt} = k \cdot (1 - \alpha)$	$0.50 < \alpha < 0.95$ A type $0.75 < \alpha < 0.95$ B type		22.1 ± 2.0 22.8 ± 2.4	8.73 ± 0.9 9.90 ± 0.6
		Single-crystals			
Power law $(n = 2)$	$\dfrac{d\alpha}{dt} = k \cdot \alpha^{1/2}$	$\alpha < 0,04$		$21.5\,(**)$	$9.6\,(**)$
"Second-order" law	$\dfrac{d\alpha}{dt} = k \cdot (1 - \alpha)^2$	$0.10 < \alpha < 0.40$		27.5 ± 2.5	12.83 ± 1.1
Modified G.B. equation	$\dfrac{d\alpha}{dt} = k \cdot \dfrac{(1 - \alpha)}{1 - (1 - \alpha)^{1/3}}$	$0.45 < \alpha < 0.83$		39.3 ± 3.4	19.35 ± 1.8

* Mean of a spread of values ranging between 13 and 30 Kcal/mole for E_a, and between 1.9 and 10.4 for log A

** Mean of a spread of values ranging between 15 and 28 Kcal/mole for E_ϵ, and between 5.9 and 13.1 for log A

iii) for powders of both types the temperature at which the decomposition starts is about the same at corresponding scan speeds; however, the temperatures at which α equals 0.5 and 1 are 10° and 15°, respectively, lower for B type microcrystals; moreover, the same kinetic laws account for the decomposition of both

A type and *B* type powders, but they are applicable to somewhat different α ranges;

iv) under the experimental conditions used, the changes of nitrogen flow and scan speed had no appreciable effect on the shapes of the thermal curves and therefore on the kinetics of decomposition; however, the runs performed without nitrogen flow (particularly those in which single-crystals were dehydrated) led to an activation energy slightly higher than the one determined in the runs with nitrogen flow. As regards the changes of sample weight, it was observed that the values deduced for the activation energies had a larger spread around the mean value for the 10 mg samples than for the 6 mg ones.

The kinetic laws, the α ranges in which they are applicable, the activation energies and pre-exponential factors are collected in Table 1 for powders of both types and for single-crystals.

2. Microscopic measurements

Etching studies on as-grown and cleavage faces of BCM were performed with the aim of determining the slip systems and of ascertaining the correspondence between decomposition nuclei and sites of emergence of dislocations on matched cleavage faces. The results were reported earlier [11]. Microscopic investigations on the thermal dehydration of BCM were performed with the aim of explaining some anomalies observed in the dehydration of single-crystals (e.g. the short period of validity of the $n = 2$ power law; see later). Runs were performed in air at constant and varying $(3 \pm 0.5°/min)$ temperature, in order to study the nucleation and the growth of nuclei of anhydrous barium chlorate on the two main as-grown faces, (011) and (110), of the crystals.

I) *Constant temperature runs.* These runs were performed by putting the crystals in the hot stage already brought to the prefixed temperature; then photographs were taken at known times. This procedure allows a safe determination of the rate of growth of nuclei, but is unreliable for establishing the rate of nucleation because of the uncertainty about the zero time and the experimental difficulty of photographing the very beginning of the nucleation. The results collected on the kinetic parameters for growth have already been reported [11], and it is only necessary to specify that the rate of growth of a nucleus in a particular direction appeared constant at constant temperature.

II) *Varying-temperature runs.* The difficulties met in determining the rate of nucleation in constant *T* runs were overcome by means of increasing-temperature runs starting from room temperature; the nucleation rate constants for the dehydration on the above mentioned faces were determined in each run, evaluating the number of nuclei at different temperatures. Plotting this number against temperature, from the slopes at particular temperatures and the corresponding numbers of nuclei, the rate constants and the activation energies could be deduced. In fact, from the equation $n = (Kt)^2$ we deduce
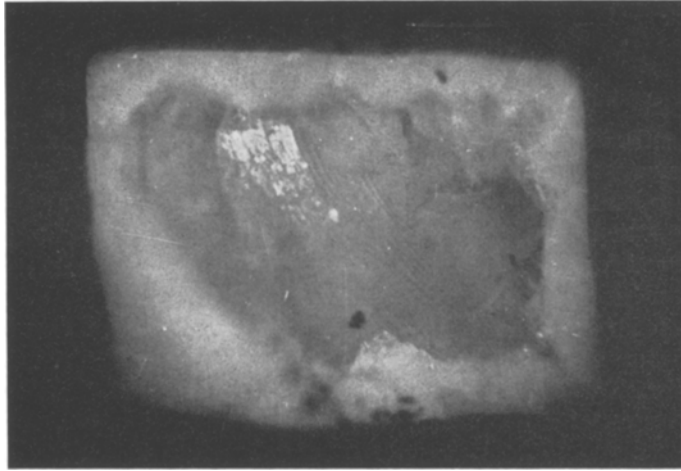
Fig. 2. BCM partially reacted single-crystal, cleaved parallel to (001). (Magn. $\times 60$)

$$n^{1/2} = Kt$$

$$\frac{1}{2} n^{-1/2} \, dn = K \, dt$$

$$dn/dt = 2Kn^{1/2}$$

If $\quad dn/dt = dn/dT \cdot dT/dt = dn/dT \cdot \Phi$, we can write

$$\ln dn/dT = \ln K + \frac{1}{2} \ln n + \ln 2 - \ln \Phi$$

$$\ln K = \ln dn/dT - \frac{1}{2} \ln n - \ln 2 + \ln \Phi$$

According to this procedure, it was possible to deduce a value for the activation energy of nucleation of about 12 ± 2 kcal/mole on both faces.

Varying-temperature runs were also used to check the results obtained for growth from constant-temperature runs. According to the shape of nuclei on the (110) surface, both longitudinal and transversal rates of growth were determined, while for the circular nuclei on the (011) face, the rate of radial growth was measured. For the activation energy a spread of values was obtained for the three cases, ranging from ~ 10 to ~ 30 kcal/mole; however, at the same temperature, the rate constants for radial growth on (011) and for transversal growth on (110) were almost equal, and lower in value than that for longitudinal growth on (110).

Some microscopy runs were allowed to go beyond complete surface dehydration. Subsequent cleavage of these crystals in directions parallel and perpendicular to the C axis showed a contracting envelope type dehydration (Fig. 2).

Discussion

The computer elaboration of the thermal data showed that for both powders and single-crystals the initial portion of the reaction is explained by an $n = 2$ power law. The acceleratory period is more extended for B type powders, thus explaining the apparently higher reactivity of such microcrystals (see iii) above).

As regards single-crystals, in some instances it was very difficult to ascertain from the thermal curves the existence of an initial power type mechanism, owing to its very short duration. Moreover, a large spread of values for the activation energy and frequency factor was obtained (see Table 1). The above phenomenon was understood on the basis of microscopic measurements at varying temperatures, which showed that the growths of different nuclei on the same surface may exhibit different temperature dependences. Such differences are far more evident when the growths of nuclei on the same crystallographic surface of different crystals are compared.

According to microscopic observations, the decomposition takes place starting from a relevant number of nuclei which grow rapidly enough. Adding the activation energies for nucleation and growth, we get the mean value deduced for the activation energy from the power law portion of the thermal curves; therefore, the spread of values reported in Table 1 for single-crystals is thought to depend on the spread of values determined by microscopy.
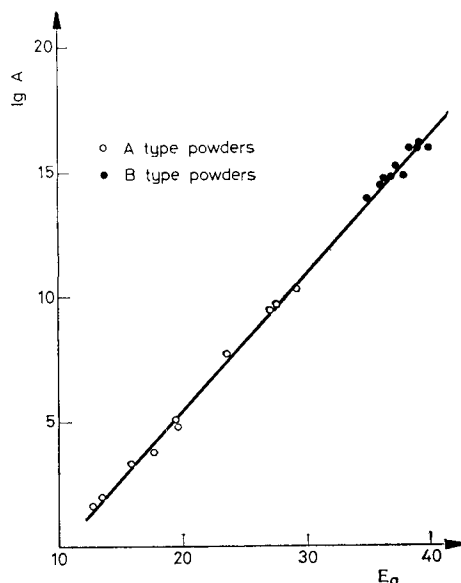

Fig. 3. Plot of log A vs. E_a for A type and B type powders, related to the central portion (Avrami—Erofeev law) of the dehydration

The fact that on (110) the nuclei grow faster along the [001] direction than along the [1̄10] one may be explained in terms of a greater reaction probability along [001], the activation energy being almost the same in both directions. This was interpreted according to the disposition of water molecules in the crystals [11].
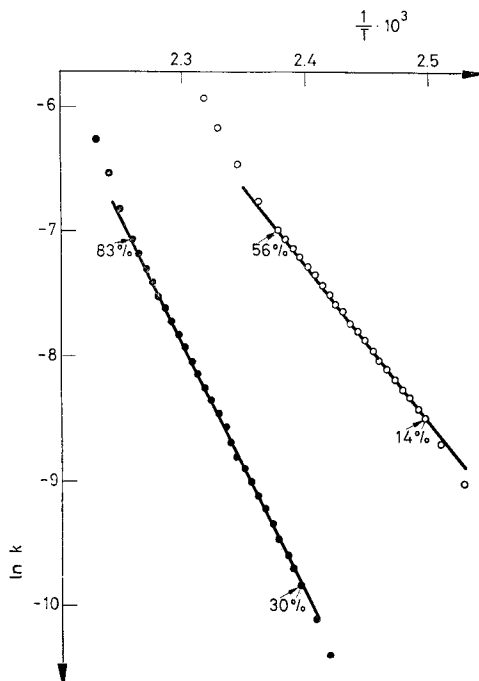

Fig. 4. Typical Arrhenius plot for the thermal dehydration of BCM single-crystals:
● : modified G.B. equation, ○ : "second-order" law, (α ranges are also indicated)

In the central portion of the reaction for powders of both types, the Avrami—Erofeev ($n = 2$) law fits the thermal data remarkably well. However, beyond the difference in the range of α in which the above law is applicable, a great difference between the two types of powders is observed as regards activation energies and frequency factors (Table 1). This discrepancy is not easily amenable to a straightforward interpretation. However, remarkable compensatory behaviour is observed when the spread of activation energies and frequency factors found for A type powders is plotted in the usual $\log_{10} A$ vs. E_a diagram (Fig. 3). It is noteworthy that the corresponding Arrhenius parameters for B type powders fall exactly on the same line, even if in a rather narrow range. This seems to indicate that the different behaviour of the powders is strictly related to the relative difference in defect content brought about by the slightly diversified preparation.

In the central portion of the reaction of single-crystals ($0.10 < \alpha < 0.45$) the best fit to the experimental data is given by second-order kinetics (Fig. 4), the parameters of which are listed in Table 1. This law is rather uncommon in the decomposition of solids; however it is justified as a special case of the Avrami
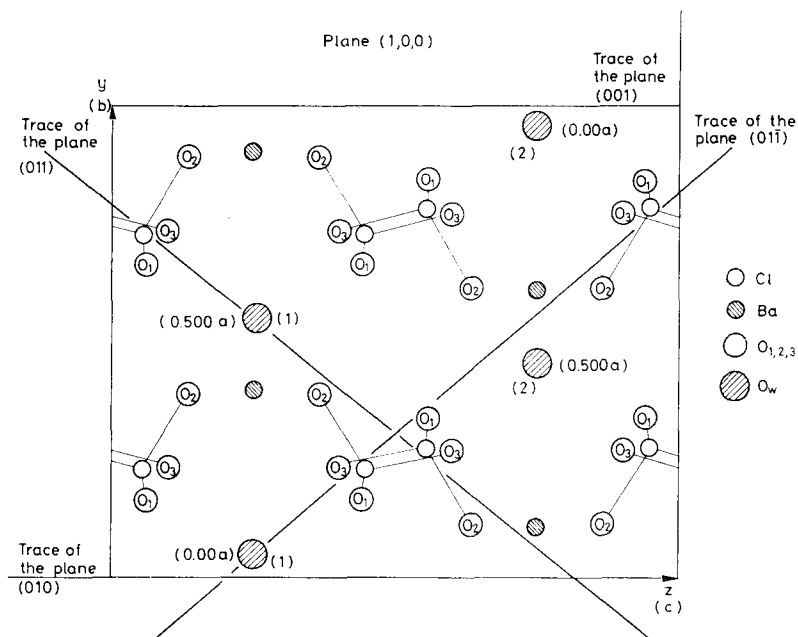

Fig. 5. Projections of the BCM structure: a) on (100): the dislocation $1/2 \{111\} \langle \overline{2}11 \rangle$ brings the water molecule (1) in correspondence of (2), underneath the plane of the drawing; (Heights of water molecules are indicated between brackets)

law [12] under the conditions that the new phase is fine-grained and the overlap is small. The apparent discrepancy between microcrystalline powders and single-crystals is therefore approximately reduced to an effect of crystal dimensions.

However, a recrystallization phenomenon of the product phase seems to take place in single-crystals, giving rise to a somewhat protecting layer through which the gaseous product has to diffuse. In fact, for the range $0.45 < \alpha < 0.8$ the computer elaboration gives a strong indication that the parameters m, n and p of the general Sestak and Berggren [1] equation:

$$d\alpha/dt = K\alpha^m \cdot (1 - \alpha)^n \cdot [- \ln (1 - \alpha)]^p$$

take the values $m = 0$; $n = 2/3$; $p = -1$. The term $[- \ln (1 - \alpha)]^{-1}$ is characteristic of processes in which diffusion is interfering, and is equivalent [1] to the term

$$[(1 - \alpha)^{-1/3} - 1] = (1 - \alpha)^{1/3}/1 - (1 - \alpha)^{1/3}$$

which is the $f(\alpha)$ function of the differential form of the Ginstling—Brounshtein (G.B.) equation. Thus, the kinetic law applicable to BCM single-crystals in the above mentioned α range is:

$$d\alpha/dt = K(1 - \alpha)^{2/3} \cdot [(1 - \alpha)^{-1/3}]^{-1} = K \cdot \frac{1 - \alpha}{1 - (1 - \alpha)^{1/3}}.$$

(see Fig. 4). Such an equation may easily be obtained if, in the deduction of the G.B. equation (see e.g. Pannetier and Souchay [13]), the concentration of the diffusing species, instead of being constant, is assumed to be proportional to the
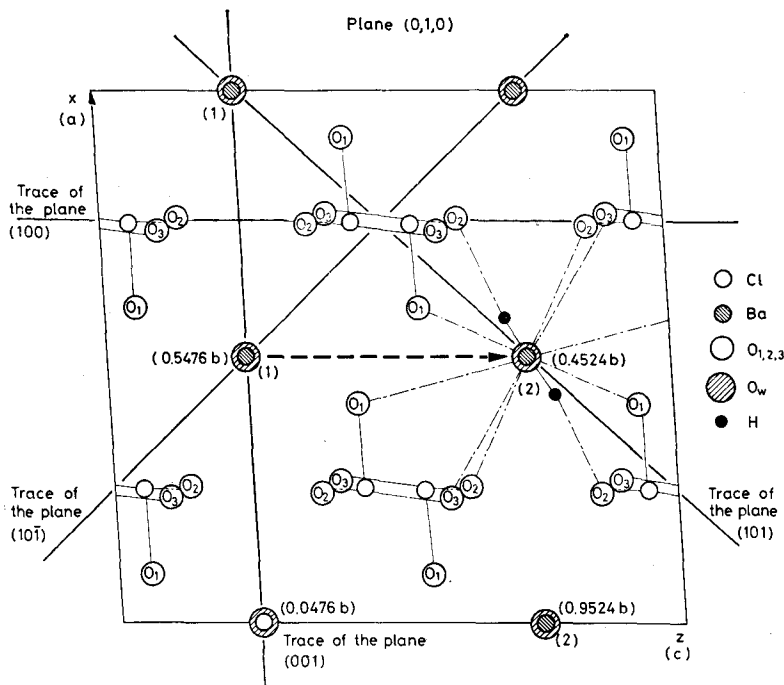

Fig. 5. b) on (010): the dislocation 1/2 (010) [001] is shown by the arrow; the dislocation 1/2 {101} ⟨Ī11⟩ brings the water molecule (1) in correspondence of (2) above the plane of the drawing.

extension of the surface of the unreacted material, that is to $(1-\alpha)^{2/3}$. This involves the hypothesis that the diffusional process remains quasi-stationary. However, a sound mechanistic interpretation of the above empirical rate law is not easy. We may only guess that the number of water molecules at disposal for diffusion per unit surface of the reactive interface (which should be constant independently of the reactive surface extension) decreases with the interface. As there is

microscopic evidence [11] that the reaction takes place preferentially at dislocation sites (e.g. by the mechanism shown in Fig. 5), the above could imply that the reaction goes on through the formation of new dislocations in the unreacted material. If some sort of repulsion (see e.g. Weertman and Weertman [14]) between dislocations is assumed, preventing the formation of new dislocations within a certain distance from a preceding one, then the number of water molecules per unit surface at disposal for diffusion might well decrease with the extension of the interface.

Conclusions

The thermal dehydration of BCM takes place through a rather complex succession of different kinetic steps. These are correctly revealed by differential scanning calorimetry if careful experimentation is used. However, some results could not have been understood without the help of an independent source of information. The use of optical microscopy was of primary importance in the present instance; as an example, the spread of values of the activation energy found for single-crystals in the acceleratory region was an effect of the fact (revealed by microscopy) that the growths of different nuclei on the same surface may show different temperature coefficients. This aspect of the thermal dehydration of BCM is of particular interest and deserves further work.

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RÉSUMÉ — La cinétique de la déshydratation thermique du chlorate de baryum monohydraté en poudres microcristallines et en monocristaux, a été étudiée par analyse calorimétrique différentielle (DSC). L'évaluation des données thermiques par ordinateur a montré qu'une seule loi cinétique n'était pas applicable à l'ensemble de la décomposition; de plus, dans le cas des poudres, on doit appliquer des lois différentes de celles des monocristaux dont la réaction paraît être limitée, vers la fin de la déshydratation, par la diffusion. La microscopie optique a été largement utilisée comme source indépendante d'information afin de clarifier certains résultats thermiques et d'acquérir une connaissance plus profonde du mécanisme probable de la réaction.

ZUSAMMENFASSUNG — Die Kinetik der thermischen Dehydratisierung mikrokristalliner, Pulver und einzelner Kristalle von Bariumchlorat Monohydrat wurde mittels Differential-Abtastkalorimetrie untersucht. Die Computerverarbeitung der thermischen Angaben zeigte, dass für die vollständige Zersetzung nicht ein einziges kinetisches Gesetz gültig ist, sondern, dass für Pulver, bzw. für einzelne Kristalle, deren Reaktion gegen Ende der Dehydratisierung als diffusionsbegrenzt erscheint, verschiedene Gesetze eingesetzt werden müssen. Als unabhängige Informationsquelle wurde die optische Miskroskopie weitläufig eingesetzt um einige thermische Ergebnisse zu klären und eine tiefere Einsicht in den möglichen Reaktions-mechanismus zu gewinnen.

Резюме — С помощью дифференциальной сканирующей калориметрии была изучена кинетика термической дегидратации микрокристаллических порошков и монокристаллов моногидрата хлората бария. Компьютерная обработка термических данных показала, что единственный кинетический закон не объясняет всего разложения, а различные законы должны быть использованы для порошков и для монокристаллов, где кажущаяся реакция определяется диффузией к концу дегидратации. Широко использована оптическая микроскопия, как независимый источник информации, для выяснения некоторых термических результатов и более глубокого проникновения в сущность реакционного механизма.