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THE KINETIC STUDY OF ISOTHERMAL SOLID STATE DECOMPOSITIONS. THE INFLUENCE OF SAMPLE VARIABLES

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ABSTRACT

For reactions which proceed by a contracting-interface mechanism, the intractability of the rate equation often leads researchers to assume a value for the "order", n. The assumed value (usually either 0, 1/2, 2/3, or 1) which gives the best fit to the experimental data is then used to characterise the mechanism and to determine the rate constant, k. Since these assumed values of n correspond only to simple theoretical considerations of the geometric advance of the interface and not to any critical experimental observation, the validity of this approach is questionable. In the present study, we use the non-linear least squares method of data analysis, reported previously, to obtain (simultaneously) optimal values of both k and n. We report how these optimal values vary with the experimental conditions, e.g. sample mass, particle size, etc., for the dehydration reactions of strontium hydroxide octahydrate and of strontium formate dihydrate. The applicability of a contracting-interface mechanism to these reactions is supported by thermoanalytical/kinetic studies, and in the latter case, also by microscopic examination.

INTRODUCTION

An earlier study by Judd and Norris [1] in this department concerned the dehydration of the octahydrates of barium and strontium hydroxides. On evacuation at ambient temperature, these materials dehydrate, without an induction period, at a rate which decreases continuously throughout the course of reaction. These features and also reduced-time plots [2] suggest that dehydration proceeds by a contracting-interface (C.I.) mechanism according to the rate equation ($n \neq 1.0$) [1,3]

$$1-(1-\alpha)^{1-n} = kt(1-n) \qquad (1)$$

In this expression, α is the fractional decomposition at time t, while k and n are the rate constant and so-called "order" of reaction, respectively. Equation (1) reduces to

$$1-(1-\alpha)^{1/2} = \frac{kt}{2} \qquad (2)$$

and

$$1-(1-\alpha)^{1/3} = \frac{kt}{3} \qquad (3)$$

when n assumes values 1/2 and 2/3, respectively. These values have been given [4] theoretical significance since eqns. (2) and (3) may be deduced from geometric considerations regarding the shape and movement of the reaction interface. The value $n = 1/2$ corresponds to the interface moving as a contracting disc, while $n = 2/3$ corresponds to a contracting sphere.

In general, reaction is unlikely to proceed exactly as predicted by the above equations, which correspond to an idealised model for decomposition [5—7]. Hence, the theoretically significant values of n will not necessarily be encountered in practice. It is therefore clearly desirable to analyse the kinetic data by a method which avoids the need to assume a fixed value of n. Several numerical methods are available for this purpose [3,8]. Of these, the non-linear least squares (NLLS) approach can be recommended since it provides reliable and statistically objective values of the kinetic parameters as well as their standard deviations. Additionally, the NLLS method can be extended [9,10] to analyse isothermal mass change data directly using the modified form of eqn. (1)

$$C_t = C_\infty + (C_0 - C_\infty)[1 - kt(1 - n)]^{1/(1-n)} \tag{4}$$

where α is identified as the fraction $(C_0 - C_t)/(C_0 - C_\infty)$ and values of C are sample masses measured experimentally as transduced chart readings. Here, the subscrips 0, t and ∞ imply initial, instantaneous and final readings, respectively, obtained under identical conditions.

Now, deviations of experimentally determined values of n from the idealised values may be due to (a) random and/or systematic errors inherent in the experimental method, (b) inadequacy of the method of data analysis, (c) inapplicability of the C.I. mechanism, or (d) uncontrolled sample variables. In a previous paper [10] we recommend procedures, adopted here, which minimise or allow for factors classified under (a) and (b). Hence, we are now primarily concerned with points (c) and (d). The earlier work of Judd and Norris [1] indicated that the dehydration of strontium hydroxide octahydrate was a contracting-interface process. This view is supported by kinetic studies discussed later. However, the particulate nature of the material makes it difficult to provide additional, independent, evidence to validate the C.I. mechanism. Further, particulate samples do not facilitate the control of sample geometry. Hence, we have also studied an alternative system involving strontium formate dihydrate. In contrast to the hydroxide, this material can readily be prepared as large single crystals with a well-defined geometry. The crystals are translucent and this enables the early stages of reaction to be observed under the microscope. Such observations provide additional information on the suitability of the C.I. mechanism to the dehydration reaction.

For both systems, we exploit the accuracy and objective nature of the NLLS method to reveal how sample variables such as mass, particle size and shape influence the values of k and n. The results clearly supplement the earlier work by Judd and Norris [1] and aim to identify those features which are of most importance to the interpretation of kinetic data.

EXPERIMENTAL

Materials and methods of sample preparation

Strontium hydroxide octahydrate

Stock samples of this compound were prepared from the salt $Sr(OH)_2 \cdot 8 H_2O$ [minimum assay (acidimetric) 97%] supplied by British Drug Houses Ltd. This material was mechanically sieved into five particle size ranges: 1.20—0.85, 0.85—0.60, 0.60—0.42, 0.42—0.30 and 0.30—0.21 mm diameter, using BS 410/1962 mesh sieves.

For experiments with pelleted samples, ca. 18 mg quantities of 0.60—0.42 mm material were compacted by hand pressure into 5 mm diameter thin discs using a tablet press.

Strontium formate dihydrate

Single crystals of this material were deposited on standing from a solution of strontium formate prepared by reacting strontium carbonate with formic acid as described elsewhere [11]. (TG experiments indicate the crystals have the formula $(HCOO)_2Sr \cdot 2 H_2O$.) Twinned, oversize or badly flawed crystals were subsequently dissolved in the re-heated stock solution to provide a further supply of crystals; water additions were made when necessary to make up for losses due to evaporation. A small quantity of formic acid was also added as a precaution against hydrolysis of the formate ion. Both the original and re-formed crystals were dried on filter paper and, in common with the hydroxide stock samples, were stored in stoppered tubes until required.

Thermoanalytical methods

Both the formate and hydroxide materials were analysed by thermogravimetry (TG) and by differential thermal analysis (DTA). The latter analyses were carried out using a Stanton Instruments Standata 6-25 apparatus, both at reduced pressure and under flowing nitrogen gas at ambient pressure. using a heating rate of 10 K min^{-1}. Single crystals of the formate were diluted with powdered alumina reference material to improve the thermal contact with the sample container.

Thermogravimetric analyses involved a Stanton Redcroft TG-750 thermobalance. Samples weighing typically 8 mg were heated at 10 K min^{-1} under flowing nitrogen gas.

Further experimental details, where appropriate, accompany the figures presented later.

Kinetic methods

Kinetic data were obtained from isothermal mass change experiments. For the hydroxide, a C.I. Electronics model 2B microbalance was employed with the sample limb maintained at constant (298.2 K) temperature by a thermostatted water jacket. Dehydration of 1—70 mg samples was initiated by reducing the pressure within the balance assembly by means of an Edwards rotary pump. Experiments initially involved a shallow dish-shaped aluminium container (15 mm × 3 mm), but in later studies a smaller hemispherical (5 mm radius) sample pan was used.

Experiments involving the reduced pressure dehydration of strontium formate dihydrate required elevated temperatures. We therefore used the TG-750 in its isothermal mode. This instrument provides rapid initial heating of the sample to the study temperature (363 K). The balance system was pumped from both above and below the sample container to minimise problems associated with pressure, buoyancy changes etc. [10]; the system pressure was maintained essentially constant at ca. 0.15 mm Hg by means of a controlled leak of nitrogen gas. Since, at elevated temperatures, the value [in eqn. (4)] of C_0 at the reaction temperature may differ from the value measured experimentally at ambient temperature [10], the latter value was optimised numerically during the data analysis.

Microscopic methods

Microscopic examination of strontium formate dihydrate crystals during dehydration was achieved using a Leitz "Metallux" microscope having a hot-stage attachment. Photographs were taken at ca. 3 s intervals using 35 mm Kodak high-speed (400 ASA) film in conjunction with a Leica SLR camera incorporated in the apparatus. A high contrast developer was also employed to give good photographic definition.

Because of the translucent and highly reflective nature of the crystals, the viewing window (aligned perpendicular to the axis of view) was replaced by a thin glass window, mounted at an angle of ca. 30°, in a machined aluminium block. The glass—metal seal was effected by means of picein wax. A vacuum-tight seal between the block and the hot-stage was achieved by using an O-ring smeared with vacuum grease.

The hot-stage was heated progressively to ca. 420 K by manual adjustment of the current flowing through the heater. The temperature of the hot-stage was monitored by a Comark Electronics "electronic thermometer".

RESULTS AND DISCUSSION

Strontium hydroxide octahydrate

Thermoanalytical studies

DTA curves for strontium hydroxide octahydrate are shown in Fig. 1. For a nitrogen gas atmosphere at ambient pressure, the curve shows three largely superimposed peaks corresponding to dehydration and agrees closely with the curve reported by Berrgren and Brown [12]. In contrast, under reduced pressure conditions (comparable with those adopted for kinetic studies), only a single dehydration peak is observed. This suggests that all the water molecules are evolved concurrently.

TG curves corresponding to each of the five stock samples, and obtained

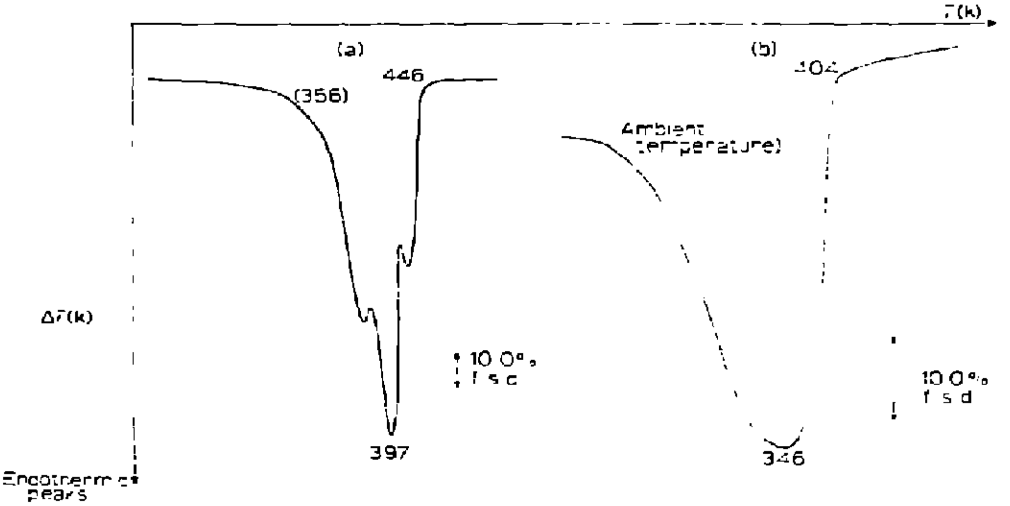


Fig. 1. DTA curves for strontium hydroxide octahydrate. Heating rate 10 K min^{-1}; 100 μV f.s.d (a) 80 mg sample, 300 cm^3 min^{-1} nitrogen, (b) 60 mg sample, continuously evacuated. Temperatures in parentheses are extrapolated onset temperatures. All other temperatures are either peak temperatures or temperatures at which peaks terminate.

using a flowing nitrogen purge gas at ambient pressure, indicate a mass loss of between 52.1 and 50.2% over the temperature range ca. 325—400 K. These values may be compared with 54.2% for complete dehydration of the octahydrate. All the curves show a point of inflection which corresponds approximately to the monohydrate. Both this inflection and the slight discrepancy between experimental and theoretical mass losses are more pronounced for the lower particle size samples. The latter feature suggests that slight water loss from the smaller particles may have occurred prior to analysis. At the same time, the more pronounced point of inflection observed for the smaller particles indicates that, near the end of reaction (when the evolved water has to pass through a comparatively large bulk of product material), diffusion control may need to be considered. For this reason, we analyse data only up to $\alpha = 0.9$.

Kinetic studies: range of data

Under reduced (ca. 0.15 mm Hg) pressure conditions, isothermal (298.2 K) mass change experiments show that dehydration commences without an induction period at a rate which decelerates throughout the course of reaction. No point of inflection is observed and, over the region ca. $0.3 \leqslant \alpha \leqslant 0.9$, (t, α) data conform closely with eqn. (1) corresponding to the C.I. mechanism. Optimal values of n predicted by the NLLS method of data analysis lie within the range 0.3—0.5 as detailed later. Over the range ca. $0.0 \leqslant \alpha < 0.3$, eqn. (1) appears unsatisfactory in that inclusion of these early data during the analysis frequently causes an increase in the reduced error sum of squares function

$$Q(k, n) = (1/P) \sum_{i=1}^{P} (\alpha_{i,e} - \alpha_{i,c})^2 \qquad (5)$$

(In this equation, the subscripts e and c correspond to experimental and calculated values of α_i, respectively, over $i = 1, 2, ..., P$ sets of data.) This increase in $Q(k, n)$ may simply reflect the disproportionally greater error due to more rapid reaction in the early stages of decomposition. On the other hand, Fig. 2 shows that a typical set of experimental (t, α) data conforms closely ($\alpha <$ ca. 0.3) with the first-order rate equation

$$\ln(1 - \alpha) = -kt \tag{6}$$

This aspect of the work requires additional study and will not be discussed further in this paper. However, it is clear that if the C.I. mechanism does not apply in the initial stages of reaction, it would be wrong to include early data in the analysis with that model. Nevertheless, in practice, the errors introduced in k and n are fairly small in the present case. For example, the data represented in part in Fig. 2 lead to values $k = 0.0564(1)$ and $n = 0.358(3)$ for the range $0.32 \leqslant \alpha \leqslant 0.90$, but to values $k = 0.0566(1)$ and $n = 0.363(4)$ over the wider range $0.60 \leqslant \alpha \leqslant 0.90$. More significant differences are observed when there are fewer and more widely spaced data.

A useful strategy to identify the range over which the C.I. mechanism applies involves a series of "repeat analyses" in which early data points are successively rejected, to establish a minimum value of $Q(k, n)$. [An erroneous point can lead to a local minimum, so it is wise to ensure that the following three successive values, say, of $Q(k, n)$ are in fact higher.] This strategy indicates that, in general, the suitable range is given here by $0.30 \leqslant \alpha \leqslant 0.90$. In some cases, more of the early data are rejected, but in this event the values of k and n differ only very slightly from the values which correspond to the wider range quoted. However, it is only over the optimised range that

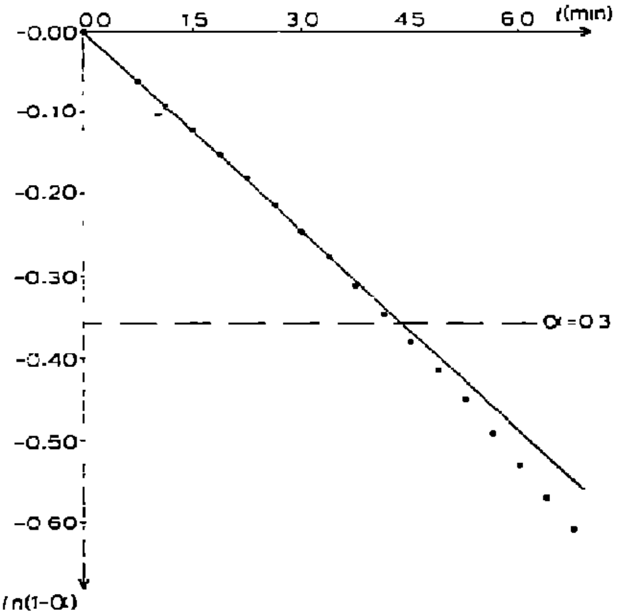


Fig. 2. Plot of $\ln(1-\alpha)$ vs. t for the early stages of decomposition of strontium hydroxide octahydrate.

the residual values $\alpha_{i,e} - \alpha_{i,c}$ have an apparently random distribution of sign (positive or negative); for the wider range, the signs are often grouped into alternate blocks of positive and negative values. The latter feature suggests a slightly distorted fit [1].

Kinetic studies: sample variables

Reproducibility between experiments. Analysis of the data ($0.3 \leqslant \alpha \leqslant 0.9$) from a series of isothermal (298.2 K) mass change experiments involving ca. 7 mg (0.60—0.42 mm) samples of strontium hydroxide octahydrate lead to mean values, $k = 0.0966 \pm 0.0018$ min^{-1} and $n = 0.438 \pm 0.009$. The fairly low standard deviation about the mean quoted for each parameter reflects the satisfactory reproducibility between experiments. For any single NLLS analysis, the standard deviation in the estimate of k is ca. 3% of the absolute value of this parameter and is generally ca. 2% less than the corresponding deviation predicted for n. The greater precision of the estimate for k is in accordance with earlier predictions [8]. The quality of the fit of predicted and experimental data is indicated by the low values (around 4×10^{-5}) of $Q(k, n)$ obtained [see eqn. (5)].

Influence of sample mass (M). The effect of varying the sample mass, but maintaining a constant (0.60—0.42 mm) particle size, upon the kinetics is shown by the results presented in Table 1. The value of k is observed to decrease significantly with increasing sample mass, while n follows a similar, although not entirely consistent, trend. The variation in k may be caused by self-cooling effects due to the endothermic nature of the reaction [13]. In this event, as Fig. 3 confirms, k is unlikely to vary directly with M, but rather upon the exact shape and size of the sample heap. Unfortunately, the present experiments provide no means of relating these variables with the sample mass.

TABLE 1

Effect of sample mass on the isothermal (298.2 K) dehydration of sieved (0.60—0.42 mm) samples of strontium hydroxide octahydrate at reduced pressure (ca. $0.3 \leqslant \alpha \leqslant 0.9$)

Sample mass (mg)	k (min^{-1})	n [a]
70.2	0.0232 (1)	0.373 (7)
55.5	0.0277 (1)	0.345 (8)
40.3	0.0339 (2)	0.320 (8)
18.0	0.0567 (1)	0.375 (3)
10.0	0.0801 (1)	0.434 (3)
7.0	0.0966 (3)	0.438 (5)
1.0	0.1821 (4)	0.459 (4)

[a] Numbers in parentheses indicate mean standard deviations calculated during the NLLS analysis, e.g. 0.0232 (1) = 0.0232 ± 0.0001; the experimental values of k and n quoted in this and following tables are mean values from at least 2, and generally 4—5, separate experiments.

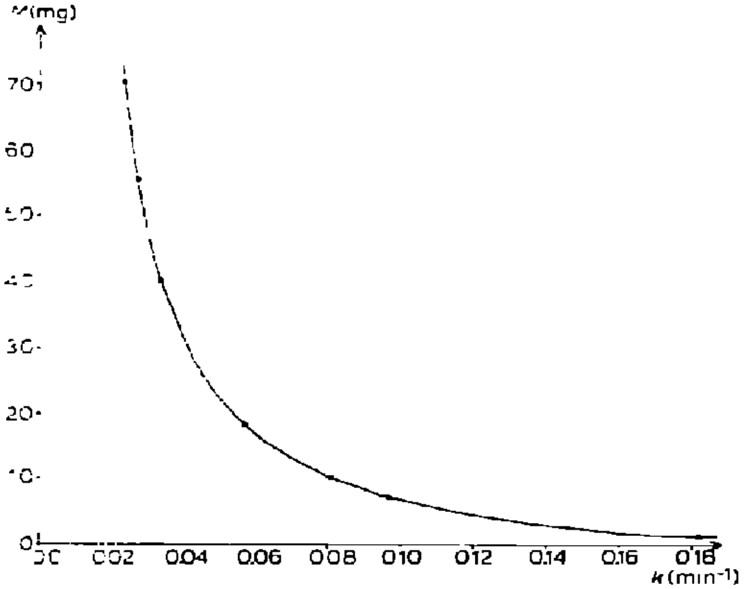


Fig. 3. Variation of the rate constant, k, with sample mass, M, for the isothermal dehydration of strontium hydroxide octahydrate.

At present, we are uncertain as to the correct interpretation of the results for n. However, it seems likely that this parameter also depends upon the precise sample geometry. Thus, in general, an increased value is observed as the sample mass, and hence also the degree of heaping, decreases.

Influence of particle size. The effect of particle size upon the kinetic parameter values is demonstrated by the results presented in Table 2 for 18 mg samples. In general, both k and n are seen to increase with decreasing particle size, although unexpectedly high values are shown for the largest particle size material. Considering k first, an increased value may be expected for smaller particle size samples due to the increased surface area/volume ratio for reac-

TABLE 2

Effect of particle size on the isothermal (298.2 K) dehydration of 18 mg samples of strontium hydroxide octahydrate at reduced pressure (ca. $0.3 \leqslant \alpha \leqslant 0.9$)

Particle size (mm)	k (min^{-1})	n
1.20—0.85	0.0541 (1)[a]	0.502 (4)
0.85—0.60	0.0499 (1)	0.350 (4)
0.60—0.42	0.0567 (1)	0.375 (3)
0.42—0.30	0.0667 (2)	0.412 (4)
0.30—0.21	0.0733 (1)	0.490 (3)

[a] Experiments with the coarsest material were generally less reproducible; the value quoted is the mean of four experiments with standard deviation about this mean of ± 0.0026.

tion. In this event, the seemingly anomalous value of k for the coarsest material may be due to the increased importance of gaps between the particles, which allow a comparatively greater surface area of particles within the sample to be exposed.

Again, the correct interpretation of the results for n is uncertain. However, it is interesting to note that high values of n are shown by both the coarsest material, which necessarily involves very few individual particles, and by the finest material for which the sample is closely packed. It seems probable, therefore, that the observed value of n reflects both how the interface progresses through the individual particle and also through the bulk of the sample.

Form and dimensions of the sample container. Experiments carried out using 18 mg samples of 0.60—0.42 mm diameter particles show that the mean value of k decreases from 0.057 min^{-1} to 0.028 min^{-1} when the dish-shaped sample pan is replaced by the hemispherical container described previously. In contrast, the mean value for n (= 0.354) is not significantly different from the previously observed value of 0.375.

The higher value of k obtained when the dish-shaped pan is employed supports previous evidence that a heaped sample appreciably inhibits the rate of reaction. Whether inhibition arises because the different sample geometry alters, for example, the importance of self-cooling, the surface area for initiation of reaction etc., or because of diffusion effects, requires further investigation.

Compacted samples. The use of pelleted samples was intended to show whether the sample geometry could be altered to provide a control over the progress of the interface through the sample. Thus, cylindrical pellets of sample might be expected to lead to the "theoretically significant" values 0, 1/2 or 2/3 according to whether reaction proceeds primarily along one or at equal rates along two or three orthogonal axes. In fact, optimal values of n were poorly reproduced and intermediate values (ca. 0.35) were usually obtained. The poor reproducibility is probably due to varying degrees of strain incorporated in the sample during compaction, causing the interface to become distorted as it proceeds through the sample. However, since the observed values lie between those corresponding to the simplest geometric interpretation, it appears that the manner in which the interface actually proceeds through the sample is more complicated than indicated by the theoretically significant values.

Compaction also leads to a much lower value of k (typically 0.036 min^{-1} compared with 0.057 min^{-1} for uncompacted samples). This result is not unexpected since the compacted samples used here exhibit a low exposed surface area/volume ratio for initial reaction while they would also be expected to increase the importance of diffusion control.

Strontium formate dihydrate

Thermoanalytical studies

Thermogravimetric analysis of single crystals (10—20 mg) of strontium formate dihydrate, using a nitrogen purge gas at ambient pressure, reveals a mass loss of 16.9% over the temperature range ca. 360—425 K. An identical mass loss, which corresponds to complete dehydration, is observed when the analysis is carried out at reduced (0.2 mm Hg) pressure, but dehydration commences at approximately 315 K. The lack of any point of inflection on the curves, even when the heating rate is reduced to 2 K min^{-1}, indicates that both water molecules are evolved concurrently.

The DTA curve (Fig. 4) obtained at ambient pressure shows a large endothermic double peak corresponding to dehydration. The appearance of these two peaks suggests, in the light of TG and microscopic evidence (see later), that water in the liquid phase is first evolved and this then evaporates. Conversely, at reduced (ca. 0.25 mm Hg) pressure, only one dehydration peak is observed and hence it appears that, under these conditions, the water is evolved directly in the vapour phase. For this reason, kinetic studies were also carried out at reduced pressure.

Microscopic studies

Microscopic examination of large (ca. 50 mg), partially dehydrated, single crystals of strontium formate dihydrate shows that water loss causes the crystals to become opaque. At an early stage, an opaque layer is formed on all faces of the orthorhombic crystal, indicating that reaction does not occur preferentially at certain crystal planes. This layer becomes thicker as reaction proceeds and it is clear that further dehydration involves an inner core of hydrated material, which appears to be of similar shape to the original crystal. These observations suggest that reaction probably proceeds by a contracting-interface mechanism. Unfortunately, since the outer opaque layer prevents observation of the interface during reaction, we are unable to draw any conclusions concerning the rate of interfacial advance or (since cleavage of the

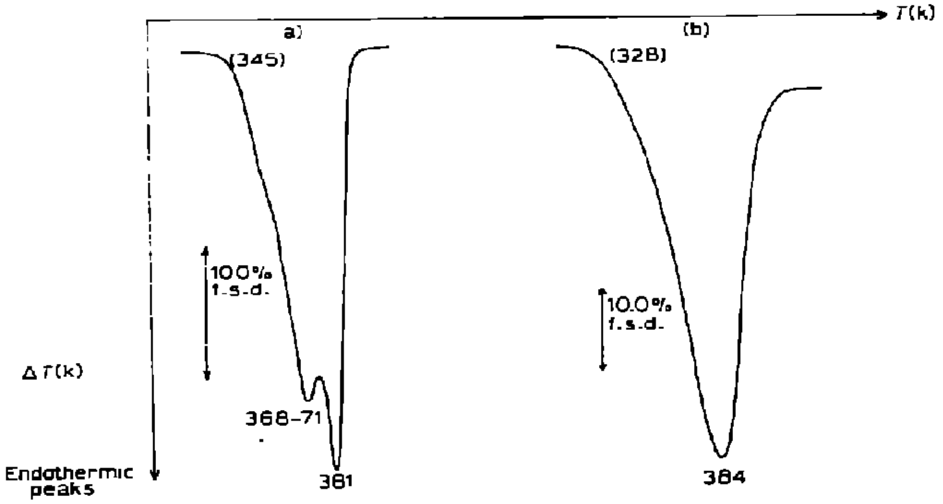


Fig. 4. DTA curves for strontium formate dihydrate (50 mg samples diluted with 40 mg alumina reference material). Heating rate 10 K min^{-1}; 100 μV f.s.d. (a) 500 $\text{cm}^3\ \text{min}^{-1}$ nitrogen, (b) reduced pressure (ca. 0.25 mm Hg).

crystal caused it to break up) whether the interface is entirely coherent.

Much of the crystal surface contains large numbers of stepped reactangular, or pyramid-like projections, as shown in Fig. 5(a), covered by translucent and featureless material which prevents optical measurement of their height. Under both ambient and reduced pressure conditions, minute fissures appear at temperatures around ca. 350 K; these fissures cover the entire surface and not apparently just distinct sites. They do not enlarge in size as reaction proceeds, but instead become more numerous [Fig. 5(b)]. Under reduced pressure conditions, further reaction is evident only by the increasing opacity of the crystal. In contrast, at ambient pressure (particularly when rapid heating is involved) water bubbles appear at the surface of the crystal [Fig. 5(c)]. These bubbles, which are most apparent at about 410 K, confirm that formation of liquid water is occurring more rapidly than evaporation.

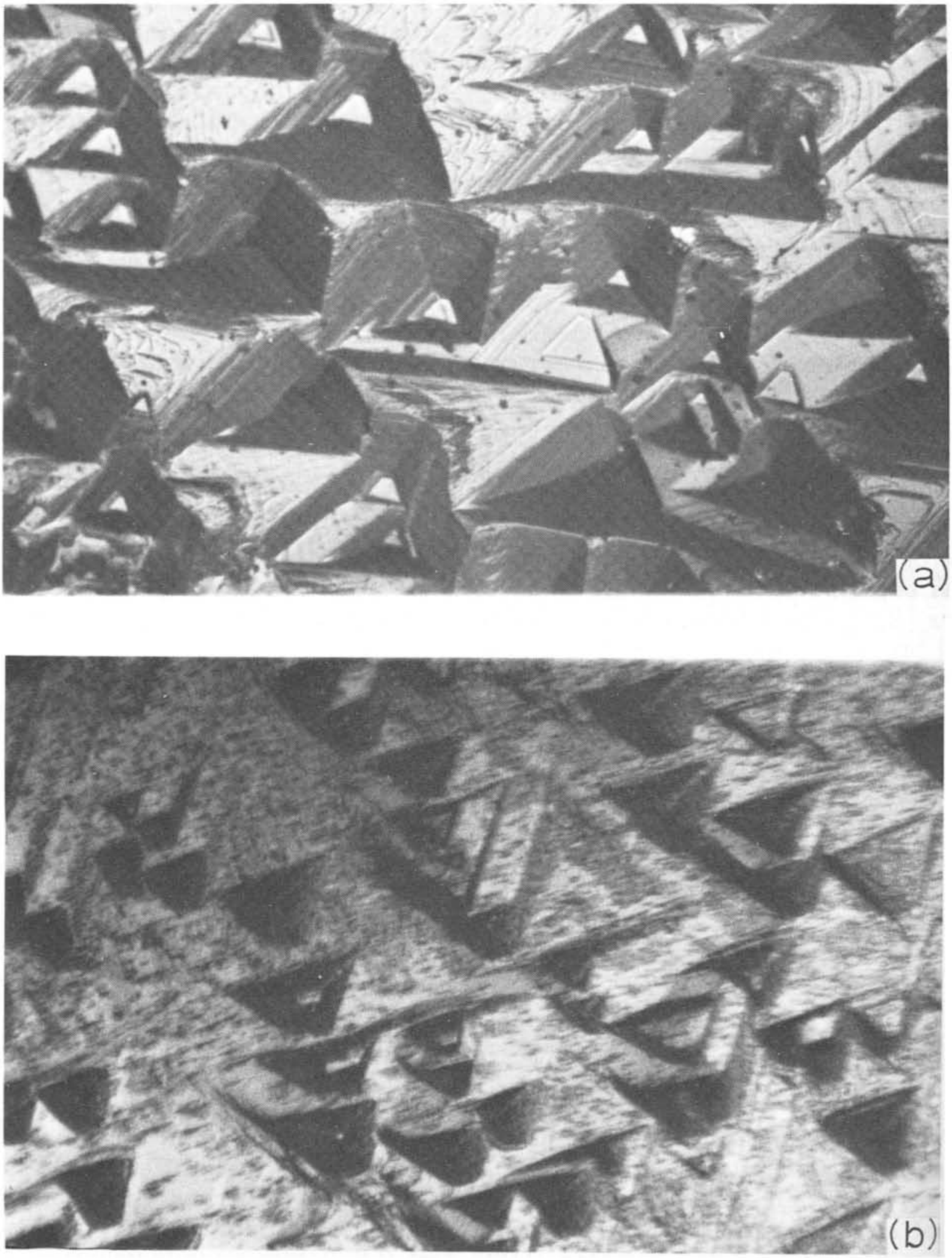
The above observations provide strong support for the previous interpretation of the DTA curves for this material.

Kinetic studies

Reproducibility between experiments. Preliminary analyses of isothermal mass change data indicate that, out of the commonly applied rate expressions [2,4]. the contracting-area model [corresponding to eqn. (1) with $n = 0.5$] provides the best fit. The applicability of a contracting-interface mechanism is supported further by the microscopic evidence presented previously and by the shape of the (t, α) curves, which show a continually decreasing rate of reaction (cf. the strontium hydroxide system).

The analysis of five similar sets of data obtained from experiments involving ca. 8.5 mg single crystal samples leads to mean values $k = 0.0414 \pm 0.0022$ min^{-1} and $n = 0.369 \pm 0.021$. Comparison of these kinetic parameter values and their corresponding standard deviations with those obtained for the strontium hydroxide system shows that the reproducibility between experiments is poorer in the latter case. This feature is attributed to variations in the physical nature of the different crystal samples employed. Such variations may be due, for example, to differences in lattice strain, crystal defects etc. It is probable that, in powdered samples, many of these differences are "averaged out", and hence kinetic studies appear more reproducible.

Influence of sample mass. The influence of sample mass upon the kinetics was investigated over the range ca. 10—50 mg, the upper limit being determined principally by the physical size of the sample pan. Samples were made up of 1—4 crystals, each weighing 10—13 mg. These experiments led to optimal values of k ranging between 0.027 and 0.077 min^{-1} while values of n were between 0.18 and 0.38. Unfortunately, the variations in these parameters could not be correlated with the number of crystals employed to make up the sample. However, the low values of n suggest that the reaction interface may develop primarily from the larger upper/lower faces of the crystals, since in the limiting case this would lead to a value of $n = 0$.



Influence of crystal size. The influence of crystal size upon the values of k and n was determined by taking differing numbers of crystals (each of similar size) to make up samples of constant (ca. 25 mg) mass. Table 3 shows the mean values of k and n obtained for samples involving 1, 2, 4 and 7 crys-

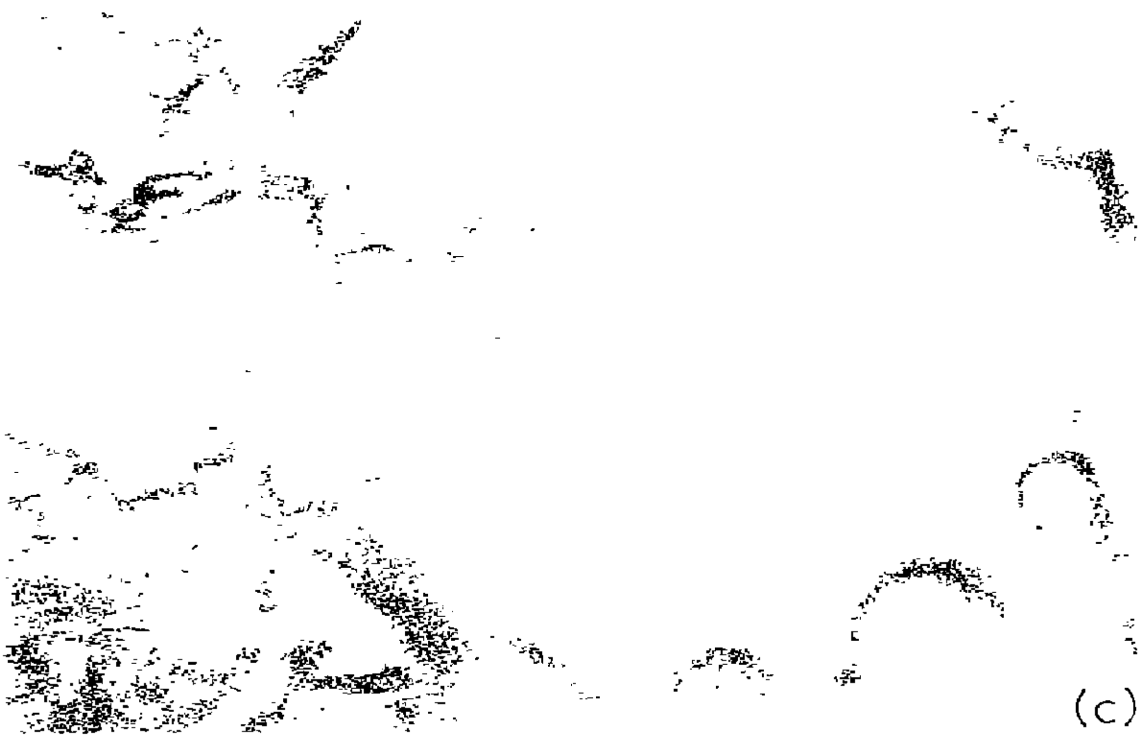


Fig. 5. Photographic investigation of the dehydration of a single crystal of strontium formate dihydrate. (a) A crystal surface in air at ambient temperature. (b) Crystal surface at ca. 350–360 K showing a large number of minute fissures. (c) Crystal surface at ca. 410 K showing the formation of water bubbles

tals. Reproducibility was found to be better in the present experiments, probably because multi-crystal samples were composed of smaller crystals which allow more even packing. In common with the findings for the strontium hydroxide system, k increases with decreasing crystal size. Again, this is thought to be due to the increased surface area/volume ratio for the smaller crystals. Values of n do not show any obvious trend although the single crystal samples lead to rather higher values

Finally, when single crystal samples are employed, so that sample packing need not be considered, k decreases significantly with increasing sample size

TABLE 3

Effect of crystal size on the isothermal (363 K) dehydration of 25 mg samples of strontium formate dihydrate at reduced (0.15 mm Hg) pressure (ca $0.25 < \alpha < 0.9$)

Mean sample mass (mg)	No. of crystals	Mean mass of each crystal (mg)	k (min^{-1})	n
25.2	1	25.2	0.0258 (1)	0.324 (8)
25.4	2	12.7	0.0266 (2)	0.240 (13)
26.0	4	6.5	0.0334 (4)	0.272 (16)
25.2	7	3.6	0.0417 (2)	0.260 (7)

TABLE 4

Values of k and n obtained from experiments involving the isothermal (363 K) dehydration of a single crystal sample of strontium formate dihydrate at ca. 0.15 mm Hg pressure (ca. $0.25 < \alpha < 0.9$)

Mean sample mass (mg)	k (min^{-1})	n
4.83	0.0439 (5)	0.286 (13)
6.39	0.0409 (7)	0.313 (22)
10.10	0.0405 (3)	0.378 (8)
25.20	0 0258 (1)	0.324 (8)

as Table 4 shows. Values of n do not follow a clearly defined trend, but since the largest crystals generally lead to the highest values, it seems likely that the results reflect the increasing thickness of the crystals, i.e. that the reaction interface proceeds more as a contracting-cube for which a higher value of n is anticipated.

CONCLUSIONS

Isothermal mass change experiments involving strontium hydroxide octahydrate have shown that the dehydration kinetics are influenced by the sample mass, particle size, shape and physical nature of the samples studied. Specifically, the results indicate that the theoretically significant values of $n = 0, 1/2, 2/3$ and 1 in the contracting-interface equation represent a very much over-simplified mechanism. In practice, intermediate values must be expected, and kinetic studies should therefore involve numerical methods of data analysis which do not require the value of n to be assumed. The nonlinear least squares approach adopted here has proved to be most satisfactory.

For the strontium formate dihydrate system, microscopic studies have provided visual evidence to support the applicability of the contracting-interface mechanism to the dehydration reaction. Again, values of n intermediate between the theoretically significant values have been encountered. We had hoped that the use of single crystals would facilitate the experimental study. In fact, although we have demonstrated the influence of sample variables, e.g. mass, crystal size etc., upon the values of k and n obtained. the system has proved to be less amenable to interpretation than was expected. It seems that while, in principle, the use of single crystals can provide more fundamental information, in practice the differing individual crystal reactivities make detailed comparisons between kinetic experiments difficult to obtain. Accordingly, it appears that, paradoxically, powdered samples may give rise to more reproducible kinetic data than can be obtained using single crystals.

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