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A kinetic and mechanistic study of the dehydroxylation of calcium hydroxide

Andrew K. Galwey * and Genevieve M. Laverty

School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland (UK)

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Abstract

A series of complementary kinetic studies of $Ca(OH)_2$ dehydration showed that the reaction is deceleratory throughout and that isothermal yield–time data were satisfactorily described by the first order equation. Arrhenius parameters and relative reaction rates are sensitive to the reactant mass and its compaction/dispersal within the reaction zone. Rates of water evolution are significantly influenced by the pressure of water vapour prevailing, the local concentrations of water vapour within the reactant mass and the rates of intracrystalline and intercrystalline escape of water vapour from the reactant assemblage.

The theoretical significance of the present observations are discussed in the context of electron microscope observations and the extensive literature already available concerned with this reaction. We formulate a reaction model that takes due account of previous proposals, for homogeneous or for heterogeneous-type mechanisms. We conclude that reaction advances inward from initial crystal boundaries but that water elimination is by diffusive loss from within an extended zone of maintained reaction crystal structure. Dehydration does not occur at a sharp reactant–product interface, unlike many solid state processes, and the kinetic characteristics are more deceleratory than the requirements of the contracting volume rate expression. Water loss is not closely followed by recrystallization; these steps are separated in space and time.

INTRODUCTION

Many of those kinetic and mechanistic studies that have most significantly contributed towards the advancement of the theory of solid state decompositions have been concerned with the reactions of a limited number of crystalline compounds [1]. Several well-characterized reactants have been selected for multiple investigations; see for example, the decompositions of (inter alia) $KMnO_4$, $CaCO_3$, NH_4ClO_4 [1] and $Li_2SO_4 \cdot H_2O$ [2]. Following this accepted practice, the present article reports a kinetic study of the dehydration of calcium hydroxide, the subject of several previous mechanistic investigations and discussions [3–14]. This

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* Corresponding author.

reactant has also been the subject of the characterization of prereactional effects; Niepce and co-workers [15–17] have reported changes in lattice dimensions and structural disorder in the temperature interval below that of reaction. Our present objective is to provide appropriate new observations for this already well known reaction to enable progress to be made towards characterizing the mechanism, which has not, as yet, been completely elucidated.

The dehydration of $Ca(OH)_2$ is reversible and the effects of variation of prevailing water vapour pressure and of particle sizes on reaction rates have been reported. The available kinetic data, however, show significant variations in the behaviour described including identification of the kinetic equation obeyed and the magnitudes of Arrhenius parameters [4, 9, 12, 13]. The mechanism of water release has been considered with reference to the reactant crystal structure [18–21]. The O–O distance in the solid (about 3.3 Å) is too large to accommodate hydrogen bonding [22]. Dehydration is believed to involve proton transfer and the water formed in the crystal is subsequently released [23]. Beruto et al. [21] provide evidence that the product CaO initially retains the dimensions of the precursor $Ca(OH)_2$ crystals, later transforming to CaO by a cooperative rather than a diffusion mechanism.

The significant differences that we found in literature reporting rate characteristics of $Ca(OH)_2$ dehydration, and rehydration, encouraged us to undertake a further kinetic study of both reactions at low water vapour pressure, under controlled conditions. The new observations include behaviour during repeated dehydration/rehydration cycles and electron microscopic observations of reactant textural changes. Our results are discussed in the context of unresolved problems concerning the mechanism of $Ca(OH)_2$ dehydration.

EXPERIMENTAL

Reactant

The powdered salt used throughout most of the rate studies was a commercial preparation (BDH Ltd.) reacted without further pretreatment. This preparation inevitably contained a small proportion of $CaCO_3$, that is expected to be inert in the temperature range of the present work (<700 K): $CaCO_3$ decomposition becomes perceptible only at >900 K [1].

Single crystals of $Ca(OH)_2$ reactant were prepared as described by Ashton and Wilson [24]. Saturated (CO_2-free) solutions of $CaCl_2$ and NaOH were maintained under an argon atmosphere and allowed to mix slowly by diffusion in a vibration-free environment. After 7 weeks, colourless hexagonal prisms (length ≤ 5 mm) of $Ca(OH)_2$ were carefully removed, briefly washed in hot water, dried for 20 min at 330 K in vacuum and stored over NaOH dessicant. These crystals contained about 14% $CaCO_3$.

Vacuum apparatus

Isothermal (±0.5 K) kinetic studies were carried out using a conventional glass vacuum apparatus in which the prevailing pressure of product water vapour was measured using a Baratron 222B absolute pressure gauge (0–10 Torr, read with an accuracy ±0.0001 Torr). This apparatus has been previously described in detail [25]. (Time, pressure, temperature) data were recorded at specified time intervals and retained in the computer memory. Facilities were provided for presentation of results as tabulated data or in graphical form to test fit to appropriate kinetic equations [1].

Thermogravimetric apparatus

The kinetics of isothermal (±0.1 K) dehydration and rehydration reactions in a nitrogen atmosphere were measured from reactant weight changes using a Perkin-Elmer TGS-2 Thermogravimetric Apparatus interfaced with a Perkin-Elmer System 4 microprocessor controller. Reactions were studied in flowing dry nitrogen or at a selected water vapour pressure, achieved by bubbling nitrogen through water at an appropriate constant temperature.

RESULTS AND DISCUSSION

Reaction stoichiometry

Yields of water determined from the pressure of product gas evolved in the known volume of the apparatus and from reactant weight losses agreed (±3%) with expectation for the $Ca(OH)_2$ content of the reactant. It has been suggested [26] that the presence of $CaCO_3$ exerts little or no influence on $Ca(OH)_2$ decomposition. Extents of rehydrations, similarly measured, were $99 \pm 1\%$ of expectation. Use of 77 and 213 K traps confirmed the complete condensation of water vapour and that there was no perceptible evolution of CO_2 (or CO). Thus the dehydration reaction studied was the reversible process

$$Ca(OH)_2 \rightleftharpoons CaO + H_2O$$

Kinetic studies

Dehydration of calcium hydroxide

Preliminary studies showed that dehydration rates were influenced by the dispersion of reactant particles within the reaction tube (3 mm diameter, sealed at one end in which the powder was retained by a loose glass wool plug). We concluded that reactant packing reduced the ease of product water escape so that some contribution from the reverse (rehydration) process resulted in an apparent diminution in dehydration kinetics. This effect was greatest at the lower temperatures studied and increased with a rise in the prevailing water vapour pressure.

Dispersed powder 10 mg samples. The most reliable kinetic data, that is, the reactant configuration identified as being least influenced by water uptake during reaction, were obtained using 10 mg samples of $Ca(OH)_2$ powder dispersed on glass wool to facilitate water escape from within the reactant mass. This isothermal dehydration, initially in vacuum, obeyed the first order equation $0 < \alpha < 0.85$ above 640 K. At lower temperatures rates systematically deviated from this relation to extents that increased as reaction temperature was diminished. From 25 experiments between 610 and 670 K the rate constants gave calculated Arrhenius parameters: activation energy $E = 145 \pm 10\ \mathrm{kJ\ mol^{-1}}$ and pre-exponential factor $A = 1.7 \pm 0.1 \times 10^{8}\ \mathrm{s^{-1}}$. (Here and throughout this paper all A and E values were calculated using the root mean square deviation formula.) Other rate equations [1] gave less satisfactory representations of the rate data.

Powder 10 mg samples. These experiments were identical in all respects with those described above except that the powder formed a loose aggregate in the reaction tube. Again results fitted the first order equation very satisfactorily (Fig. 1), $0.1 < \alpha < 1.0$ below 653 K. Rate constants agreed with those found for the more dispersed powders. Again there was a negative deviation in rate behaviour below expectation for the first order equation at low temperatures and at higher water vapour pressures.

Powder 28 mg samples. These experiments used larger masses (and volumes) of loosely compacted reactant (28 ± 3 mg). The pattern of kinetic characteristics was closely similar to those of the other experiments but rates of reaction were significantly less (by a factor of about 0.5 between 620 and 670 K). Again the first order expression satisfactorily represented the data $0.1 < \alpha < 0.8$ but with deviations at lower temperatures and higher water vapour pressures. It was shown, for the lowest temperatures studied (623–633 K) that the evacuation of accumulated water prouct during a reaction resulted in a subsequent rate enhancement in accordance with expectation for first order behaviour. After a further accumulation of water vapour, rates relatively diminished again. It is concluded that this rate reduction is due to the significant onset of the reverse (rehydration)

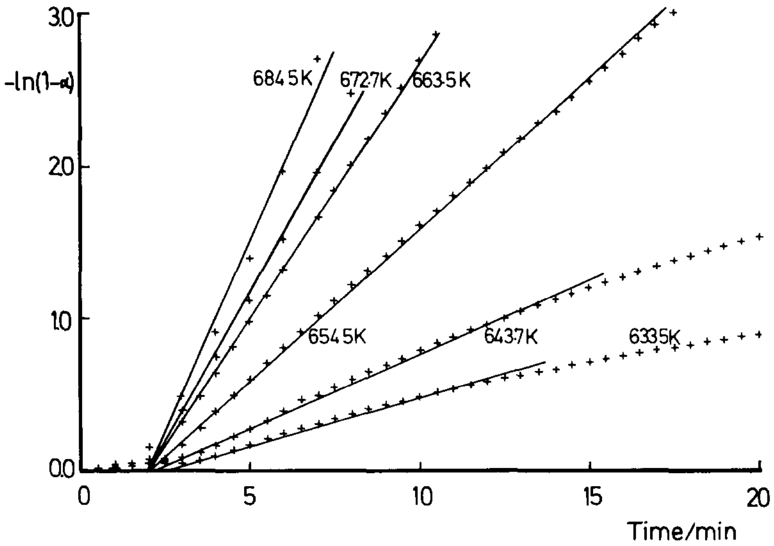


Fig. 1. Typical first order plots for the dehydration of calcium hydroxide (10 mg samples) in vacuo.

reaction; behaviour is similar to that described for ammonium chromate [27]. Arrhenius parameters calculated for these reaction conditions were $E = 174 \pm 20$ kJ mol^{-1}, $A = 6.6 \pm 1.0 \times 10^{10}$ s^{-1}.

Powder 28 mg samples in excess water vapour. Reaction conditions during these experiments were identical with those described in the previous paragraph except that a small pressure of water vapour was admitted to the apparatus before the dehydration kinetic study was commenced. The preadmission of increasing amounts of water vapour resulted in progressive diminutions of reaction rate. These are illustrated in the representative fractional reaction α-time plots in Fig. 2, dehydrations at 671 K for reactions initiated in 0, 2.6, 4.85 and 6.2 Torr H_2O. (A 28 mg sample yielded about 7.0 Torr on completion of reaction, $\alpha = 1.00$.)

The pressure dependency of reaction rate was determined from slopes of these curves at $\alpha = 0.3$, 0.5 and 0.7 together with the prevailing water vapour pressure. (Comparisons at identical α values removes the influence of the deceleratory behaviour.) The mean pressure dependency of reaction rate was found to be $P_{H_2O}^{-1/2}$ [11, 14]. Thus, unusually for a solid state reaction, the kinetic behaviour can be expressed through two concentration terms:

$$d\alpha/dt = k[Ca(OH)_2][P_{H_2O}]^{-0.5}$$

Crystal 10 mg samples. Kinetic behaviour observed for the dehydrations of $Ca(OH)_2$ individual crystals (10 ± 4 mg and area about 25 mm^2) between 633 and 673 K was closely similar to that reported above for powders. Following the evolution of a small amount of (probably surface

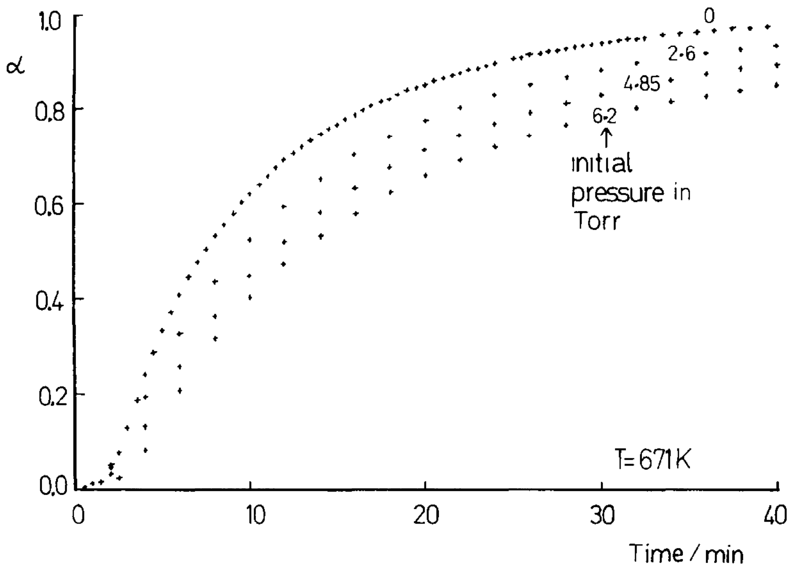


Fig. 2. Typical α-time plots for the isothermal dehydration of calcium hydroxide at 671 K in the vacuum apparatus initially containing preadmitted pressures, 0, 2.6, 4.85 and 6.2 Torr water vapour product.

retained) water ($\alpha \approx 0.03$) the first order equation very satisfactorily represented the data $0.1 < \alpha < 0.8$, see Fig. 3. Arrhenius parameters differed significantly from those of powder, $E = 76 \pm 8\,\text{kJ mol}^{-1}$ and $A = (1.6 \pm 0.2) \times 10^{-3}\,\text{s}^{-1}$. Magnitudes of rate constants were, however, comparable with those for the 28 mg powder samples in the same

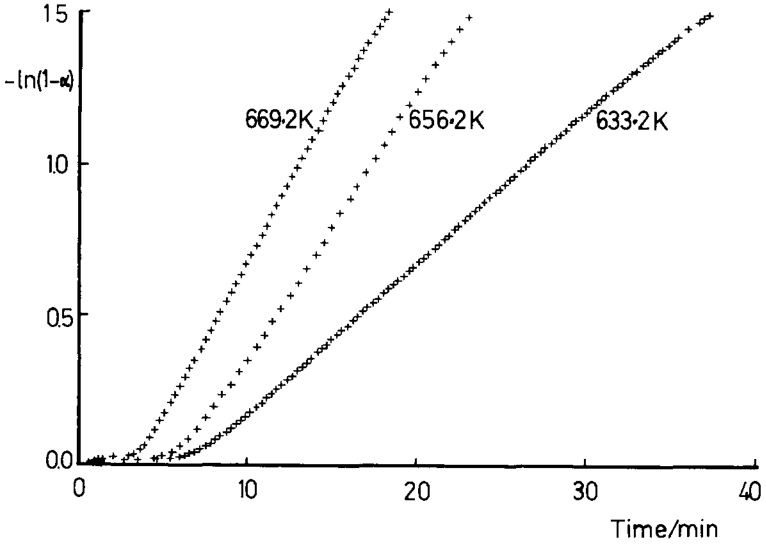


Fig. 3. Representative first order plots for the dehydrations of $Ca(OH)_2$ single crystals (about 10 mg) in vacuo.

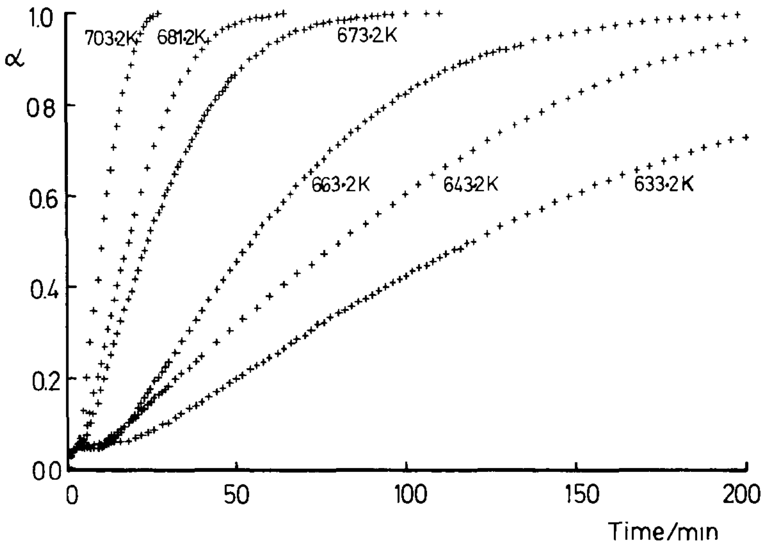


Fig. 4. Representative α-time curves for the thermogravimetric dehydration (10 mg samples) of calcium hydroxide in a nitrogen atmosphere.

temperature range. Again preadmitted water resulted in a significant diminution of reaction rate.

Powder 10 mg samples in nitrogen. Isothermal measurements of the rates of calcium hydroxide powder dehydration (5 and 10 mg samples) were studied thermogravimetrically between 633 and 703 K in dry nitrogen flowing at 6 and 12 $\mathrm{l\,h^{-1}}$. Again reactions were deceleratory, representative α-time curves are shown in Fig. 4. The first order equation was obeyed, $0.2 < \alpha < 0.7$, but no evidence of the reverse process was discerned here in the flowing atmosphere, which continually removed evolved water vapour from the reaction zone. Rate constants were, however, significantly below ($\times 0.1$) values for the reactions of 10 mg powder samples in vacuum at the same temperature and the E value was greater ($200 \pm 15\ \mathrm{kJ\,mol^{-1}}$) and $A = (2.4 \pm 0.2) \times 10^{12}\ \mathrm{s^{-1}}$. This reduction in rate and large E value is ascribed to a diminution in the ease of water product escape from within the assemblage of crystallites that constitutes the reactant.

Rehydration of calcium hydroxide

Vacuum apparatus. Most rehydration studies were completed directly following a dehydration reaction. The water vapour product was condensed at 77 K while the temperature of the reactant was reduced and equilibrated to the value at which the water uptake was to be measured. After removal of the cold trap, to volatilize the condensate (H_2O), readings were commenced.

Water uptake was a strongly deceleratory process and relatively

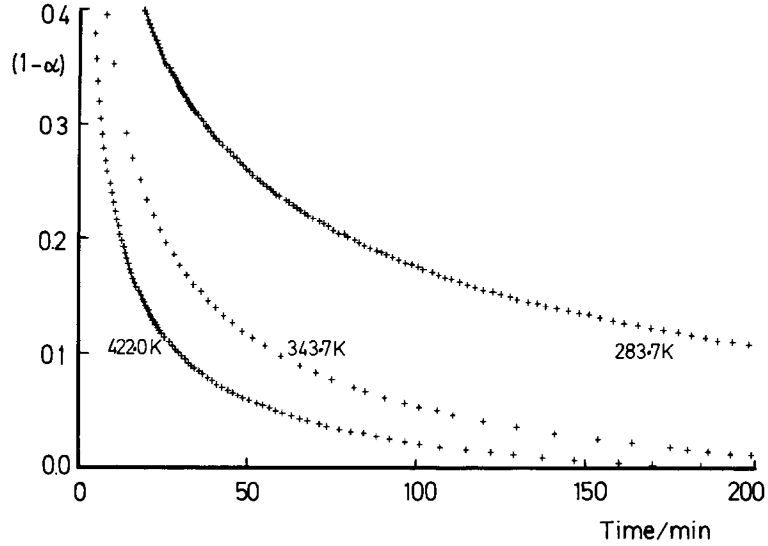


Fig. 5. Typical $(1-\alpha)$–time plots for the rehydration of 10 mg samples of dehydrated $Ca(OH)_2$ (i.e. CaO) in the vacuum apparatus across the temperature range of the present investigations.

insensitive to reactant temperature. Typical kinetic data are shown in Fig. 5 ($(1-\alpha)$ against time plots) and Fig. 6 (plots of the same data according to the Jander [1] equation). The Jander equation was selected as applicable to deceleratory solid state reactions, based on an increasing barrier layer so

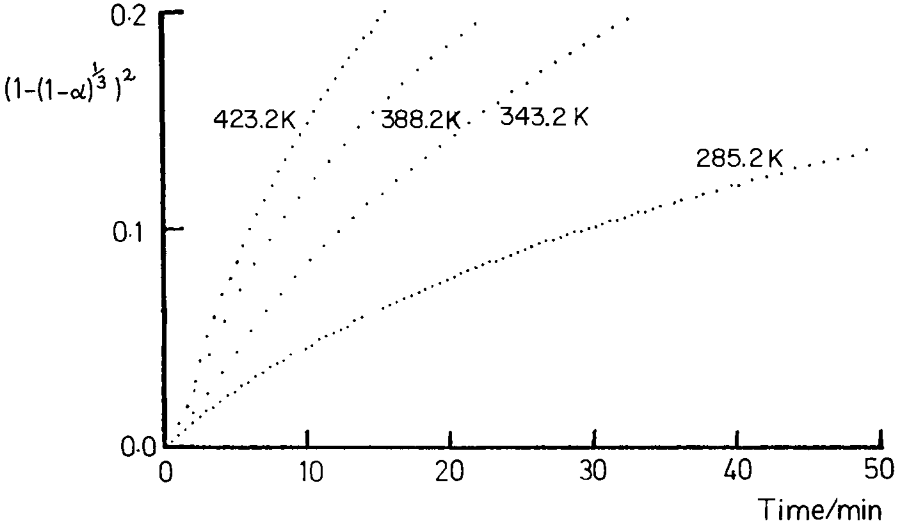


Fig. 6. Jander plots for the data in Fig. 5; reaction rates are more deceleratory than the requirements of this expression.

that diffusion across a rising thickness of product controls reaction rate [1]. Arrhenius parameters calculated from approximate Jander rate constants (there was an appreciable scatter of data) across the extended temperature range investigated, 283–473 K, were $E = 12.7 \pm 2.8\,\mathrm{kJ\,mol^{-1}}$ and $A = 1.0 \pm 0.9 \times 10^{-2}\,\mathrm{s^{-1}}$.

Comparative experiments (10 and 28 mg samples) at 292 K showed that smaller reactant masses rehydrated relatively more rapidly than larger. This suggests that interparticular diffusion within the reactant particle aggregate exerts a significant control on rate. This could be through the generation of a less easily penetrated outer compacted zone (crust) around the reactant mass.

The Jander expression includes no allowance for a rate controlling contribution from reactant gas pressure (diminishing progressively during these reactions). Comparative studies, using preadmitted excess water (above the stoichiometric requirement) showed that rehydration rates were significantly increased with larger prevailing water vapour pressures at 293 and at 471 K.

Dehydration–rehydration cycling

The rates of successive dehydrations of the same sample increased somewhat (×1.3) in consecutive reaction cycles at 613 K as illustrated in Fig. 7. Rates of rehydration, water uptake at 287 K, similarly increased by a

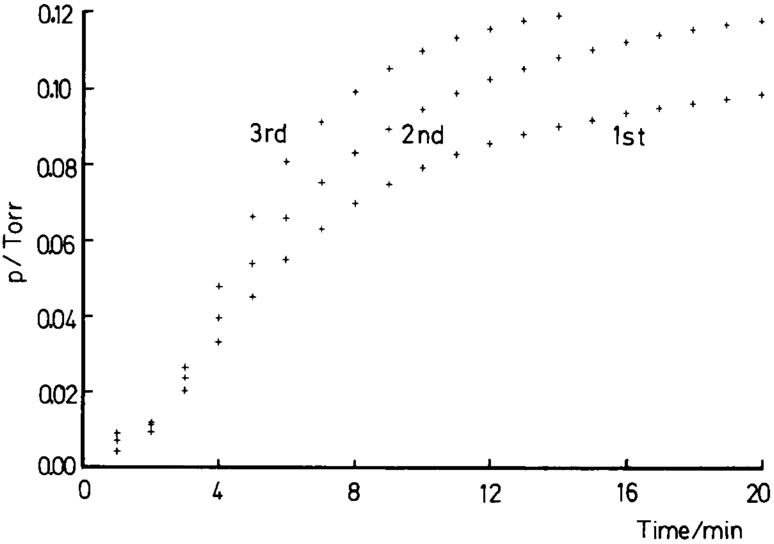


Fig. 7. Successive dehydrations of $Ca(OH)_2$, 10 mg powder samples, in the vacuum apparatus at 613 K. The rate of reaction increases somewhat in successive cycles.

comparable amount. This is consistent with the microscopic evidence that successive reaction cycles resulted in crystallite disintegration, reaction proceeding more rapidly in smaller particles.

Isotopic exchange experiments

Discussions of this reaction have considered homogeneous mechanisms within the crystal [16, 21] based on the enhanced conductivity by protons in $Ca(OH)_2$, 20–60 K below the temperature of onset of dehydration [28]. To investigate the role of these hydroxyl protons in dehydration, D_2O exchange experiments were undertaken in which the extent of D/H interchange was measured by mass spectrometry. Results confirmed exchange between D_2O admitted to the vacuum apparatus and the reactant $Ca(OH)_2$. For example there was 24% D/H exchange after 5 h at 348 K, below the temperature of the dehydration studies here. At 653 K, when $\alpha = 0.2$, the solid residue had exchanged 10% of the constituent H with D. Clearly dehydration entails a significant degree of mobility of the hydroxyl group protons and the retention of deuterium from D_2O, incorporated within the solid, is direct evidence of the concurrent participation of the reverse (rehydration) reaction under these dehydration conditions.

Microscopic studies

The considerable reactivity of the solid reaction product (CaO) with water vapour and CO_2 made microscopic studies particularly difficult because transfer from vacuum apparatus to microscope required exposure to the atmosphere. However, with careful handling, some significant textural features were characterized.

Examination of the original powder reactant in the scanning electron microscope showed it to consist of irregular crystallite aggregates, approximately 1–5 μm diameter; parallel features are attributed to its layered structure [18]. On dehydration, the habits of the $Ca(OH)_2$ were largely unchanged [21]. Some product particles had undergone disintegration and reaction resulted in some diminution in average crystallite size. Reactant surfaces underwent cracking and pore development during dehydration. There was no evidence, from careful examinations of partially dehydrated salt, that reaction resulted in the generation of structures recognizable as nuclei [29] or in the development of a coherent reaction interface [1].

Scanning electron micrographs of single crystals dehydrated ($\alpha = 1.00$) at 668 K showed that the product is pseudomorphic with the reactant [21]. There was, however (Figs. 8(a)–(c)) extensive cracking, predominantly in

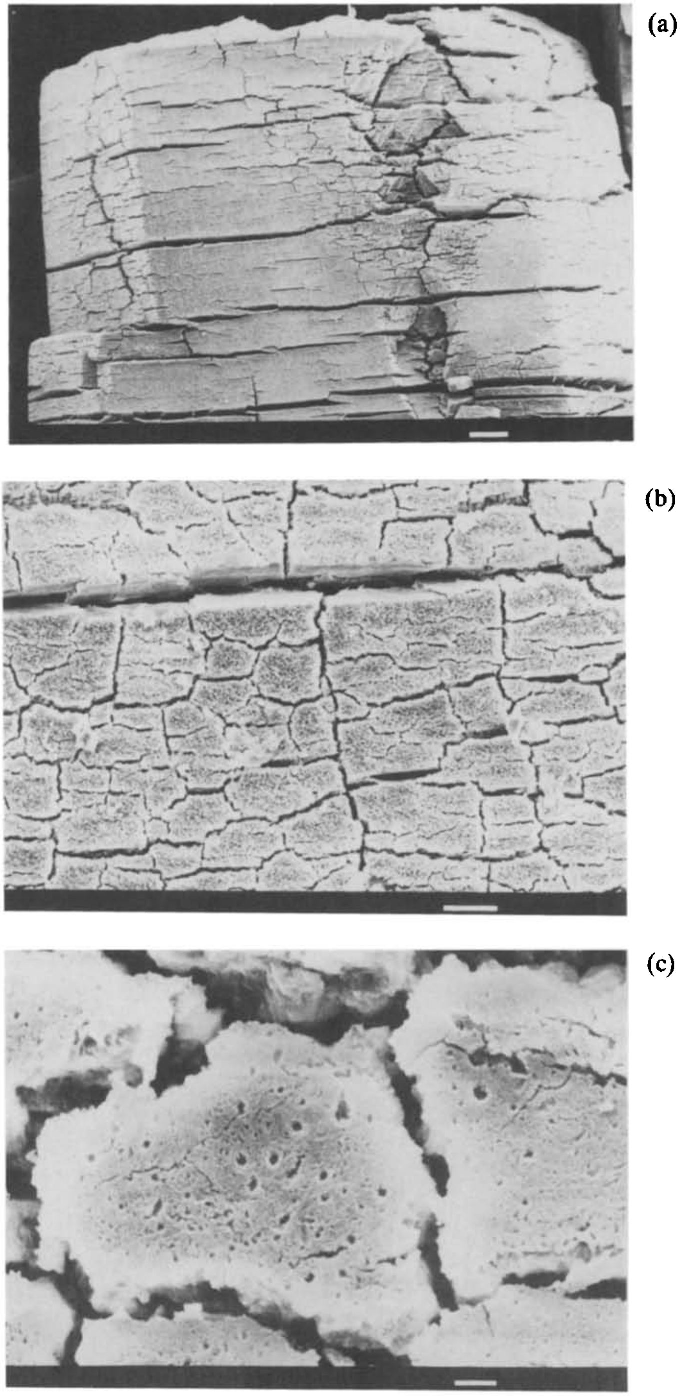


Fig. 8. Scanning electron micrographs showing the texture of a dehydrated $Ca(OH)_2$ single crystal surface ($\alpha = 1.00$ at 668 K) at three magnifications. The largest cracks are in the [001] direction, as expected from the reactant structure, but product particles are extensively cracked and penetrated by pores. Scale bars: (a) 100 μm, (b) 10 μm, (c) 1.0 μm.

the [001] direction, but also more irregularly, and crystallites were penetrated by pores.

Optical microscopic examination of [001] faces of crystals partially dehydrated ($\alpha = 0.2$ at 673 K) revealed circular crack development zones distributed on linear fault lines (Fig. 9(a)) and each consisted of a series of cracks, forking as the feature develops (Fig. 9(b)). These structures closely resemble those described as nuclei for dehydration of chrome alum [30] and possibly represent the recrystallization of product. The boundaries do not,

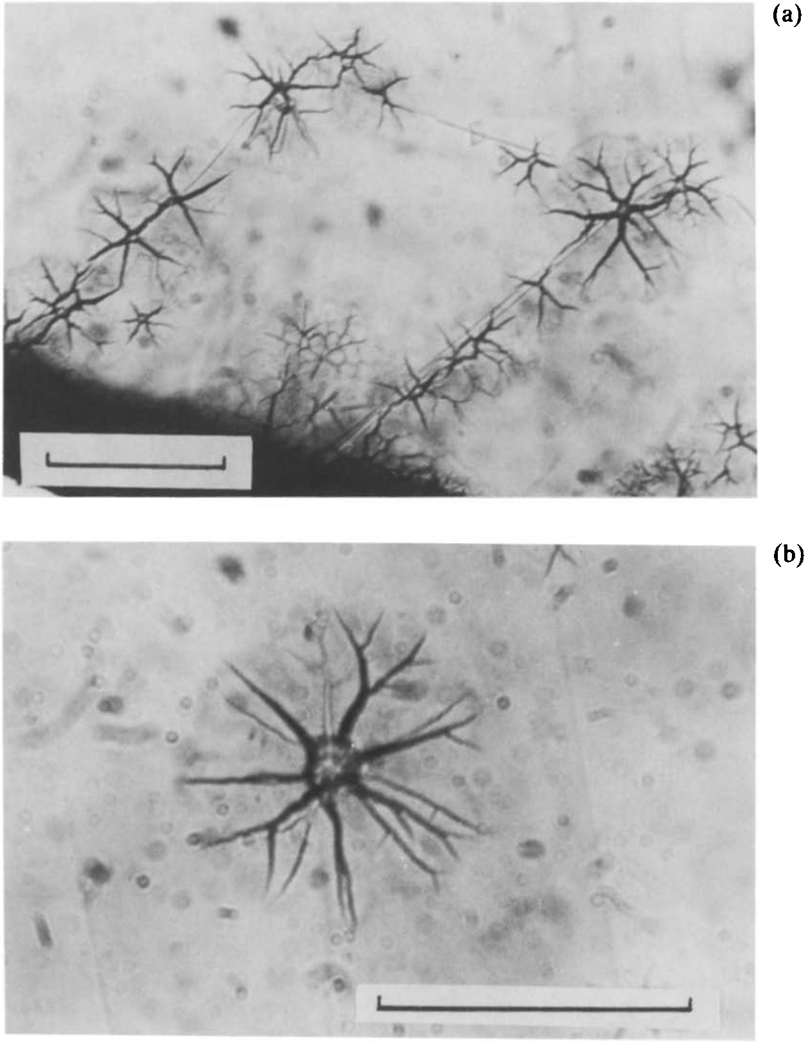


Fig. 9. Optical micrographs of crack features developed on the [001] face of a partially reacted ($\alpha = 0.2$ at 673 K) $Ca(OH)_2$ single crystal. These features are distributed along surface cracks ((a) scale bar, 70 μm) and each consists of a radiating system of cracks from a central point ((b) scale bar, 70 μm).

however, necessarily represent a dehydration reaction interface, if homogeneous type dehydration occurs in the structure and there is later recrystallization of the product phase in zones from which water has been lost.

DISCUSSION

Background to kinetic analyses

The dehydroxylation of $Ca(OH)_2$ ($\rightarrow CaO + H_2O$) is deceleratory. There was no evidence of any initial acceleratory process. Accordingly, our kinetic analyses here have been concerned with establishing whether the measured yield-time data are more accurately represented by the contracting volume, the contracting area or first order rate equations [1], following previous kinetic analyses for this solid [4, 5, 11, 13]. A more precise representation by either the contracting volume or the contracting area equations would provide evidence that the reaction proceeds by a heterogeneous mechanism. This could be interpreted as water elimination at an active reactant $Ca(OH)_2/CaO$ product interface [5, 11, 12], initially rapidly generated across all surfaces and advancing thereafter into unchanged material. Alternatively, if the kinetic fit is more satisfactorily in accordance with the first order equation, then this may be accepted as consistent with a homogeneous mechanism [8, 9]. The concentration dependence is a reaction rate proportional to the total quantity of water remaining. On this model the reaction would be regarded as the random release of water throughout the reactant crystal.

Dehydration is reversible and the distributions and dispersals of $Ca(OH)_2$ crystallites influence the ease of water escape through the interparticular and intraparticular channels of CaO product. The present observations are consistent with literature results [31] in showing that the kinetic characteristics (rate expression obeyed and calculated Arrhenius parameters) vary significantly with changes in conditions prevailing in and around reactant particles. Parameters identified as influencing reaction rate include the pressures of water vapour and of inert gases present, the particle sizes, the total mass and packing (compaction) of reactant. All of these influence the ease of diffusive escape of water from the reactant assemblage.

Hitherto, no study of the dehydration of $Ca(OH)_2$ has established reaction conditons that exclude a rate controlling influence from the reverse process: see for example the reversible $CaCO_3$ dissociation [32]. Reported A and E values show significant variations, that may be a consequence of the diverse reaction conditions adopted within the various individual studies [4, 5, 9, 10, 12, 13, 26]. From a literature survey we find values of E to vary between about 34 and 190 kJ mol^{-1}, accounting for the large uncertainty in our estimated (but meaningless) "mean" value 128 ± 53 kJ mol^{-1} [31]. However, despite these inconsistencies, kinetic measurements were largely completed in the temperature interval 700–800 K. Reaction temperatures (appropriate for kinetic measurements) are more nearly constant than the apparent activation energy values reported, a point that is discussed further under "compensation effect" below.

We conclude, therefore, that contributions from the reverse (i.e. rehydration) reaction significantly influence the measured rates of water release. The contribution from this process is certainly not directly related to α, and can be expected to be greatest later in reaction, when the rate of water evolution is diminishing. This represents an uncertainty of unknown magnitude [2] in determining the rate law for $Ca(OH)_2$ dissociation.

A second, perhaps related, uncertainty arises in making the specific distinction as to whether a particular set of data is more satisfactorily expressed by the contracting cube or the first order equations. In a recent study of $Li_2SO_4 \cdot H_2O$ dehydration [2] the α-time values were shown to fit the contracting cube equation, but if the overall yield was increased by 10%, the same set of results were more satisfactorily represented by the first order equation. In our present study, the final yield of water may not correspond with the stoichiometric requirement: uncertainty in the final yield could account for the inconclusive kinetic analyses between these particular rate equations in the literature reports. Water may be retained on product CaO surfaces. It is also possible that a proportion of the constituent (OH^-) groups of the reactant remain in the solid at $\alpha = 1.00$. These could be trapped, isolated from neighbours, with which they cannot react, if proton transfer is prevented by product CaO formation.

Crystallographic and textural considerations

In the formulation of a reaction mechanism, the following observations should be remembered:

(i) In vacuum the original crystal structure of $Ca(OH)_2$ is retained throughout much of the dehydration process [21]. The only phases present are $Ca(OH)_2$ and CaO. Suggested intermediates of the type [$CaO \cdot H_2O$] [9, 10, 12] have been justified on thermodynamic grounds rather than from crystallographic or microscopic evidence [31].

(ii) There is an increase in proton mobility (and possibly water formation) accompanied by limited crystallographic modifications [15–17] in the temperature range below that of dehydration.

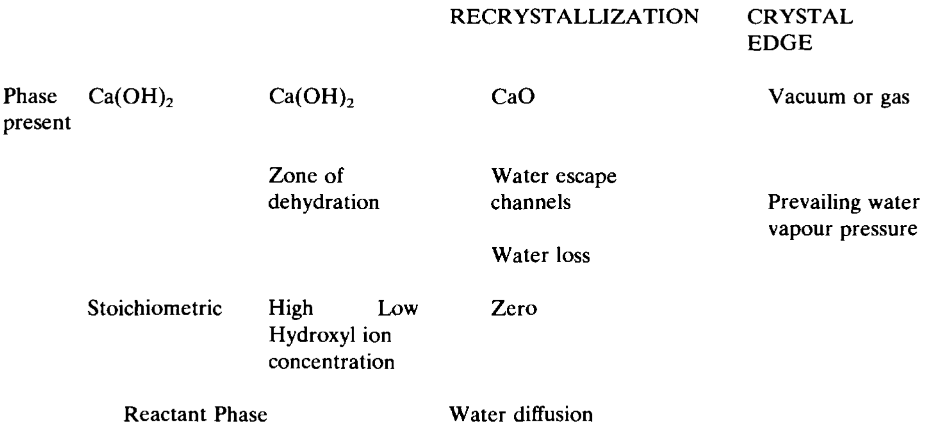
(iii) Our electron microscope observations for partly reacted powder samples gave no evidence for the participation of a reaction interface. This examination cannot, however, be regarded as conclusive because of the product reactivity together with the necessity to cool the specimen and handle in air.

Observations for the large single crystals were more useful. Crack development resulted in extensive dehydration of the reactant, Fig. 8 ($\alpha = 1.00$) though such retexturing could have occurred during cooling or subsequent handling. The radial crack systems seen in Fig. 9 ($\alpha = 0.2$) are regarded as more interesting. The appearance of these is strongly reminiscent of the nuclei formed during the dehydration of chrome alum [30, 33]. Product loss ($-H_2O$) has resulted in shrinkage of the residual solid and the opening of channels. These (Fig. 9) are generated at sites of imperfection, cracks and defects [7]. Such nuclei were not, however, apparent after similar reactions initiated in 4.3 Torr H_2O at 673 K.

Proposed reaction mechanism

Quantitative consideration of our microscopic observations (Fig. 9) show that the volumes of the CaO product nuclei (based on the circular cracked zones) are much less than expectation based on the extent of reaction (20%). Accordingly we conclude that the $Ca(OH)_2$ (reactant)/CaO (product) interface is not an active, narrow, exclusive dehydration zone during its advance into unreacted material (contracting volume model). Significant features of the observed dehydroxylation are explained by a reaction mechanism in which water is lost from the reactant by diffusive escape from solid within which the $Ca(OH)_2$ structure is maintained [21]. Subsequently, recrystallization to CaO is probably (Fig. 9) a nucleation and growth process. The essential and novel feature of this proposed mechanism is that the water release steps are not directly associated with the product recrystallization. Water loss in advance of an active, migrating interface has been described for the dehydrations of a number of other hydrates, including $Li_2SO_4 \cdot H_2O$ [34, 35], $KCr(SO_4)_2 \cdot 12H_2O$ [30, 36] and $LiKC_4H_4O_6 \cdot H_2O$ [37] but apparently the extent to which this can occur is strictly limited in these salts. We contrast this with $Ca(OH)_2$ for which the crystallographic evidence [21] and the open structure of the reactant (Ca^{2+} and OH^- ions occupy 49% of the unit cell [31]) suggest that there is relatively facile dehydration in advance of and separate from the crystallographic transformation step. Water losses with and without concurrent recrystallization have been recognized and distinguished in discussions of solid state dehydrations [38].

Essential features of the proposed reaction mechanism are shown in Scheme 1.



Scheme 1. Diagrammatic representation of the proposed mechanism of $Ca(OH)_2$ dehydration. Hydroxyl ions derived from water vapour may stabilize the partially dehydrated $Ca(OH)_2$ phase present. The CaO phase may not appear until later in reaction; during the initial stages it is not present.

The concentration distribution of hydroxyl ions within the dehydration zone may be expected to be influenced by the water vapour pressure prevailing in and beyond the escape channels. This, in turn, depends on the rate at which water diffuses through interparticulate gaps in the sample aggregate and the pressure of gases, particularly including H_2O, beyond. These pressures may depend on the rate of water release and any inert gases present which reduce ease of escape. This dependence of dehydration rate on local variations in water availability [11] raises the important possibility that reaction rates may vary inhomogeneously between individual particles within the reactant assemblage. The essential and novel feature proposed in this mechanism is the effective separation of the factors controlling water loss from the dehydration zone and those controlling product recrystallization steps. Water may be retained in the $Ca(OH)_2$ lattice and later released [15–17].

Kinetic analysis of the present data

Comparisons of data, on a composite Arrhenius plot for the present sets of first order rate constants, show that the relative reaction rates across the temperature intervals studied reduced in the sequence; 10 mg compact, 28 mg compact and 10 mg thermogravimetric reactions in an atmosphere of nitrogen. Rate constants for 10 mg samples packed and dispersed were comparable, though the latter became relatively larger at lower temperatures (with a small reduction in the apparent value of E). Under these conditions the influence of local concentrations of water vapour within the reactant mass was probably small. Rates of dehydration for 10 mg crystals were approximately half those for 10 mg powder samples and comparable with the behaviour of the 28 mg powder samples. This lower rate is attributable to the reduced ease of water escape from the more compact reactant mass (i.e. 10 mg crystals) though the activation energy was significantly less. This overall pattern of behaviour is consistent with expectation for the relative ease of escape of water vapour from within the assemblages for the various samples studied. We conclude that dehydration rates are sensitive to the locally prevailing water vapour pressure; this was also confirmed directly in otherwise identical experiments with preadmitted water vapour.

Throughout our kinetic measurements the rate equation most satisfactorily describing the observed data was the first order expression. The significant difference between this function and the contracting volume equation is the progressively more deceleratory approach to completion (at infinite time) during the final stages. (In contrast to the contracting volume expression that represents a finite completion when the interface reaches the particle centre.) We conclude, in the context of the mechanistic discussion given above, that the diffusive loss of water from within the $Ca(OH)_2$ crystal is an important reaction control. In addition, the apparent reaction rate may include a negative contribution from uptake of any water vapour present and dehydration may be inhomogeneous within the reactant mass. Accordingly, the first order obedience is ascribed to diffusive losses from the relatively thick reaction zone that progresses inward from some, or all, of the crystal faces. The dehydrated salt subsequently recrystallizes to CaO product.

The magnitude of the activation energy for the dehydroxylation reaction was not determined here, but, like some other reversible processes, varied markedly with prevailing conditions that may influence the opposing product uptake, for example $CaCO_3$ [39]. We cannot identify our calculated Arrhenius parameters with any specific step because the decomposition is complex, involving diffusion within the reactant phase, proton movement and/or H_2O [15–17] desorption and the influence of the rehydration reaction. The present calculated A and E values, for both dehydration and rehydration, do, however, exhibit a well-defined compensation effect (Fig. 10) for which the isokinetic temperature is 683 K [40]. Two further data points by Li and Bai [13], referring to this reaction <470 K and >495 K, were apparently close to this line but have been omitted because of uncertainty in their units of A. The temperature at which reaction rate constants are equal (683 K) is close to that at which the dehydration rate

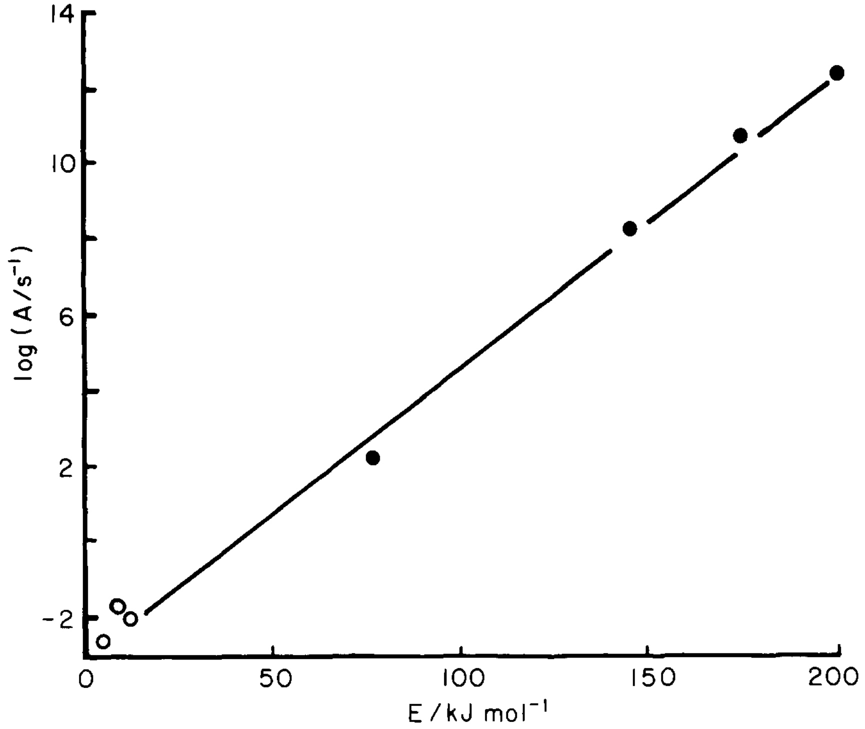


Fig. 10. Compensation plot of log(A/s^{-1}) against E in kJ mol^{-1} for dehydration (●) and rehydration (○) reactions, $Ca(OH)_2 \rightleftharpoons H_2O + CaO$. The isokinetic temperature, of equal reaction rates, is 683 K.

becomes appreciable. We conclude, therefore, that the compensation behaviour observed (Fig. 10) is a consequence of a series of reactions that become perceptible at the same temperature but for which each temperature coefficient is different because it is sensitive to the locally prevailing conditions that determine the (temperature dependent) balance between forward and reverse processes. We find no theoretical significance in the magnitudes of reported A and E values.

CONCLUSIONS

We conclude that the dehydroxylation kinetics of the reversible dissociation of calcium hydroxide are sensitive to conditions that influence the ease of water vapour product escape from the reactant mass. The first order rate equation provides the most satisfactory fit to the data. It is known [21] that the $Ca(OH)_2$ structure is maintained during the greater part of reaction. It is our belief that water loss from this structure is diffusion controlled. A dehydration zone, of significant thickness, later advances inwards from the crystal surfaces so that the rate characteristics are perceptibly more deceleratory than the requirements of the contracting volume equation. Dehydrated salt later recrystallizes to the CaO product phase but, unlike many other dehydrations, the water elimination and recrystallization steps are not closely related in space and time. The calculated Arrhenius parameters have no theoretical significance in identifying a rate limiting step but are sensitive to conditions prevailing within the reactant mass due to the influence on the forward reaction of ease of product escape and reuptake.

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