

Inorganic Compounds

STRUCTURES AND FUNCTIONS OF REACTION INTERFACES DEVELOPED DURING SOLID-STATE DEHYDRATIONS

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Abstract

The literature reveals that the mechanisms of some solid-state dehydrations are more complicated than has been generally accepted. Reactions at a thin advancing reactant-product interface provide the geometric models on which the most widely employed rate equations are based. For some systems, this "thin interface" model is a simplification of observed behaviour. Elimination of water from crystallographic sites may occur to a significant extent within a much thicker zone of reactant towards which the active interface is progressing. Consequently the region of chemical change may not coincide with the region of structural transformation. Limited initial dehydration may occur across all crystal faces prior to the onset of a nucleation and growth process that is usually regarded as the dominant rate process in the dehydrations of many large crystals. Experimental observations for solid-state dehydrations are discussed and reaction mechanisms with different rate controlling processes are distinguished. Studies of dehydrations have contributed substantially to the theory of solid-state reactivity, and advances in understanding may have wider application to other solid-state reactants.

Keywords: dehydration, hydrates, interfaces, mechanisms, solid-state reaction

Introduction

Early research into the theoretical framework governing the kinetics and mechanisms of reactions of solids relied considerably on observations for the decompositions of simple crystalline compounds [1], such as inorganic hydrates and other solids that are readily prepared in the form of large, defect free, single crystals. Theoretical conclusions and general explanations of the behaviour of these rate processes were then applied to other chemical changes involving a wider range of solid reactants.

A widely accepted concept is that in many of these reactions the chemical transformation of reactant to product occurs within an interfacial zone of locally heightened reactivity. The reactant-product interface can be regarded as a constantly advancing energy wave, within which the chemical change occurs, but the material comprising the reactant and product solids usually undergoes only minor displacements with concurrent changes in bonding. Variations in the overall rates of product formation, during the course of individual reactions, are determined by changes in the area and disposition of the interface within each solid reactant particle. Suitable kinetic expressions are formulated through consideration of the changing geometry of the interface as reaction progresses [1].

A second rate-controlling parameter, applicable in some but not all solid-state reactions, is the diffusion of a product from (or a reactant to) a reaction interface. A major objective of many studies of solid-state mechanisms is to characterize the chemistry of the interface processes and to establish reasons for the preferential occurrence of reaction within this zone.

In this paper, recent ideas concerning the role of the reactant boundary surfaces in solid-state decompositions are reviewed. This topic has been discussed previously [2], but is worthy of reexamination in the context of microscopic observations concerning the structures of reaction interfaces.

The free energy associated with crystal faces has been discussed by Jacobs and Tompkins [3]. Surface processes on solids can be detected at temperatures well below the onset of bulk reactions [4]. In many nucleation and growth processes, nucleation occurs at or close to a surface [1]. In many geometry controlled processes, reaction may be initiated rapidly across all, (or specific) reactant crystal faces and the interface generated advances into the reactant solid. In many decompositions, e.g., nickel oxalate [5], an identifiable precursor rate process (limited in extent to perhaps 1–2%) occurs in advance of the main reaction and is often identified as the breakdown of relatively less stable surface material [5].

Nucleation and growth reactions

Reactions such as the dehydrations of crystalline hydrates are not necessarily expected to proceed by a nucleation and growth process, because loss of volatile product in such dissociations would appear to occur most easily from the solid surfaces. Here the intracrystalline stabilizing forces are least effective and escape of volatile product will be least impeded. These factors are identified as important controls in all reversible reactions, including dehydrations. The theory must, however, account for the observation that the dominant chemical changes occur preferentially at the expanding boundaries of an intracrystalline nucleus located below crystal faces that have suffered little, if any, retexturing [6] apart from perforation. Escape of volatile product is through a restrictive system of (usually) narrow channels in residual product that will probably readily adsorb evolved gases in reversible rate processes.

This adoption of an apparently less favourable route to chemical change can be explained if the difficult step in enabling reaction to continue is recrystallization of

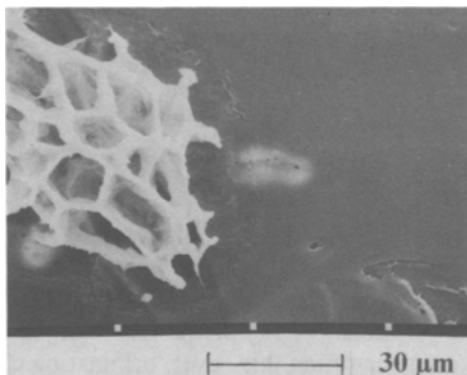


Fig. 1 Dehydration of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (loss of 5 to 6 H_2O) proceeds by a nucleation and growth reaction: the well developed intranuclear crack structures are shown in these scanning electron micrographs of replicated surfaces [6, 11]. Crack development is less pronounced in the vicinity of surfaces, as seen at the peripheries of these nuclei. This may be due to the reduced extent of retexturing within the already dehydrated surface layer

partially or completely dehydrated reactant to the stable product phase. Thus in alum dehydrations [6], water is lost rapidly initially from all reactant crystal faces but the extent (depth) to which this can proceed is limited because the unrecrystallized dehydrated material acts as a barrier to continued H_2O loss. The more efficient route for continued dehydration is the generation of the stable product phase. This phase transition is initiated at specialized (nucleation) sites. Recrystallization is the difficult step to initiate, but once achieved may continue. Opposition to escape of water is diminished by development of channels traversing the intranuclear material. The maintenance of an appreciable water vapour pressure within each nucleus may promote the recrystallization step [6, 7] (Fig. 1).

Surface properties of reactant crystals

“Orange peel textures” in some dehydrations

For many crystalline hydrates, surfaces which have been briefly subjected to conditions known to initiate dehydration (e.g. evacuation, perhaps with heating), when subsequently exposed to water vapour (e.g. 50% saturation) undergo retexturing. The appearance of the modified crystal face in the first system studied, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [6], resembled the surface of an orange, and the term “orange peel texture” has since been used as a convenient label for the phenomenon. Such roughening has been interpreted [6] as evidence that water loss from the surface introduces strain that is relieved through interaction with the vapour. Similar retexturing may occur at all advancing boundary faces of nuclei [7]. Although $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ did not generate orange peel textures [6], exposure to water vapour after some dehydration resulted in a notable increase in the number of nuclei

per unit area upon subsequent dehydration [8]. Water vapour is again identified as enhancing surface reactivity. Development of orange peel texture has been demonstrated from studies of a wide range of crystalline hydrates [9, 10], showing it to be a general, though not universal, behaviour pattern.

Unreactive surface layers

Particle faces that constitute the outer, non-advancing boundaries of the growth nuclei are, for many reactants, remarkably smooth. Such areas are much flatter than the retextured particles that constitute the intranucleus product material observed during alum dehydrations [6, 11] or the $\text{KBr} + \text{Cl}_2$ reaction [12]. (There is an essential crack system penetrating this cover, originating close to the nucleation site to permit product escape.) The lack of textural change in the 'nucleus cover' is ascribed to the completion of an early surface reaction without recrystallization, involving dehydration of alum [6], or Br_2 release from $\text{KBr} + \text{Cl}_2$ [12]. Formation of product phase can only be initiated at and continue from a limited number of nucleation sites possessing enhanced specific reactivity. Retention of some volatile product within the nucleus may promote reaction and, in particular, the phase transformation [6, 7], e.g., the covalent liquid, SnCl_4 , was identified as promoting the nucleation step in the $\text{KBr} + \text{Cl}_2$ reaction [12], where Br_2 was retained and acted as a solvent.

In other reactions, the early development of an unreactive boundary layer covering reactant particles has been described. Such material may be coherent, strong and elastic. Guarini and Rustici [13] observed bubble development during dehydration of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ and ascribed this to the pressure of steam retained within a swollen envelope composed of an impermeable boundary layer. Similar behaviour was noted during the dehydration of a hydrated copper chloride pyrimidinium complex [14]. Here rupture of the boundary layer resulted in the expulsion of a liquid identified as reactant dissolved in released water.

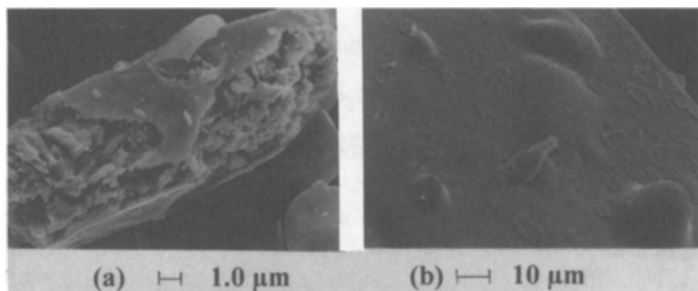


Fig. 2 Superficial unreactive "skin" on reactant surfaces.

- a) Decomposition of CsMnO_4 [19]. Crystal is covered by an outer adherent layer that is little retextured during reaction but is fragmented and detached by light mechanical abrasion.
- b) Dehydration of $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ [16]. Bubbles of steam raised on surface already scarred by previous development and bursting of similar bubbles

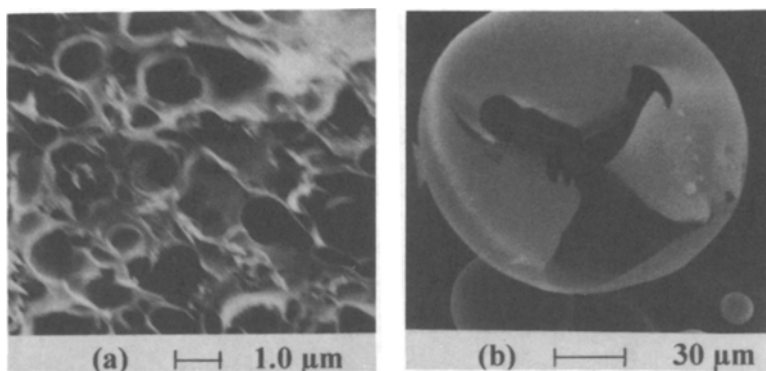


Fig. 3 Bubble formation during decomposition within a liquid phase.

- a) Decomposition of copper(II) malonate [15]. Section of partly decomposed crystal showing froth formation due to gas evolution in molten reactant.
 b) Decomposition of ammonium dichromate [20]. Burst bubble developed during gas generation within molten reactant

The early generation of an unreactive layer accounted for the absence of comprehensive melting, or extensive sintering during decomposition of copper(II) malonate [15]. Residual particles from the completed reaction were pseudomorphic with those of the reactant, despite evidence of intraparticulate melting (Fig. 2). Local surface swelling is probably due to pressure exerted by escaping gaseous products, including softening of the barrier by steam. Surface layers that can be distinguished from the material comprising the crystal interiors have been described for the dehydration of $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ [16] (Fig. 3) and the decompositions of KMnO_4 [17], RbMnO_4 [18], CsMnO_4 [19] (Fig. 2) and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, (Fig. 3) [20].

Dehydration mechanisms

For many reactants, the reactivity within the surface layer of a crystalline solid is different from, and appreciably greater than in the material beneath. From the above observations, we conclude that the overall decomposition or dehydration of a solid may proceed with two (or more) distinct controlling steps: chemical changes and a phase transformation. The chemical change may be self-inhibiting and its initial occurrence may be limited to a thin surface layer that may exhibit orange peel texture and the other 'superficial skin' properties mentioned above. The properties of such a layer appear not to be strongly influenced by the crystallographic orientation of the face because of the "real" reorganized structure of the boundary layer. The continuation of reaction necessitates the recrystallization of product phase, regarded as the difficult step. These two processes may proceed separately, perhaps some distance apart, within the reactant particle. This reaction model (Fig. 4) is discussed below with reference to dehydrations for which observations are available, to consider the roles of the two contributions to the overall elimination of water. Although there is insufficient evidence to characterize all aspects of these re-

actions, some progress has been made towards classifying dehydrations under the following headings.

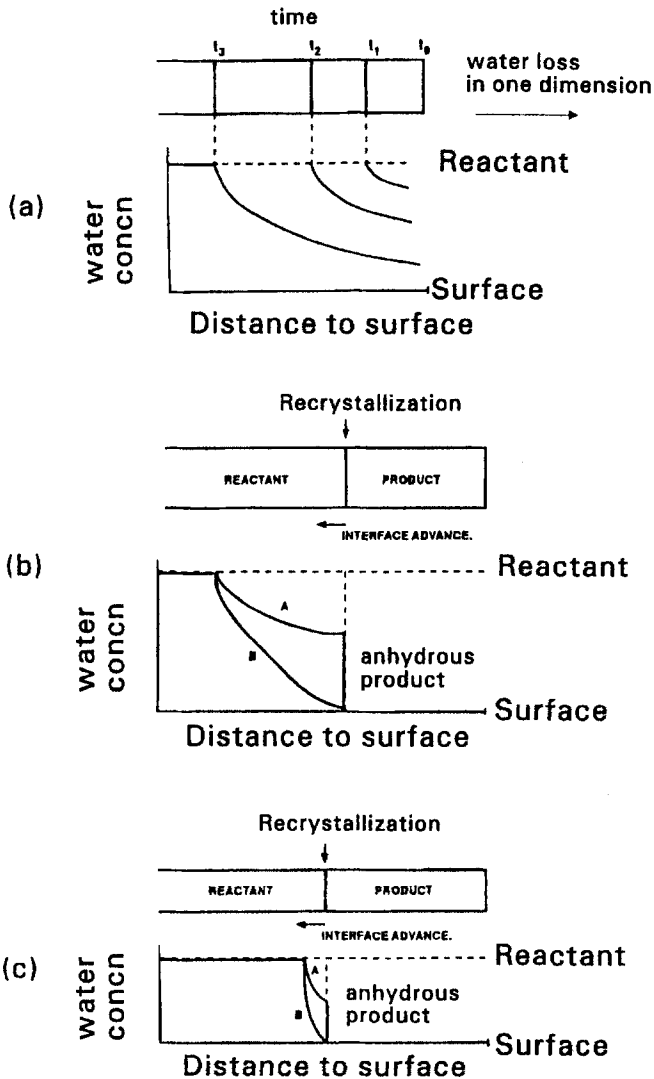


Fig. 4 Diagrammatic representation of dehydrations in which two steps: diffusive loss of water, and recrystallization of the product phase, are separated.

- a) No phase transformation – profiles of water concentration at increasing times;
 b) Loss of water followed by recrystallization of product – product is cracked permitting escape of water. Curve A: recrystallization after partial loss of water; Curve B: recrystallization after total loss of water;
 c) Loss of water closely followed by recrystallization of product. Curve A: recrystallization after partial loss of water; Curve B: recrystallization after total loss of water

No phase transformation

In many crystalline hydrates the removal of water from the solid does not generate sufficient strain to cause the reorganization of a particularly stable structure, e.g., vermiculite dehydration [21] proceeds by one-dimensional diffusive loss of H₂O from the interlayer zones. Similar behaviour has been described for a number of other layer materials [1] and zeolites. The reaction of CaSO₄·2H₂O is more complicated [22] in that there is diffusion control in the [010] direction and a chemical step in the [001] direction so that an overall topochemical model was suggested.

Water elimination followed by recrystallization of solid product

For many dehydrations, substantial, perhaps complete, water loss precedes recrystallization to the anhydrous (or lower hydrate) product phase. The geometric relationships between these different rate processes have not, as yet, been established in detail for those reactions where observations suggest that these steps are separated in space and time.

Li₂SO₄·H₂O and CuSO₄·5H₂O

Boldyrev *et al.* [23] used diffraction of synchrotron radiation to measure interplanar spacings within interface-traversing sequences of small volumes of partially reacted crystals of Li₂SO₄·H₂O and CuSO₄·5H₂O. The thicknesses of reaction interfaces were estimated to be 100–200 μm and there was a constant change of water concentration across this zone. A metastable intermediate phase was identified within the reaction zone of the copper salt.

KAl(SO₄)₂·12H₂O and KCr(SO₄)₂·12H₂O

Kinetic, thermochemical and photoacoustic studies [6, 24] of the dehydrations of these alums gave evidence of the presence of a water-depleted surface layer. The principal dehydration reaction occurred, however, at the advancing reactant-product interface that constitutes the boundaries of growth nuclei. The kinetics of the overall rate process (the Avrami-Erofeev equation, $n=2$) differed from expectation for the pattern of interface development deduced from microscopic observations. These differences may be explained by the contributions (not identified in the microscopic observations) from the occurrence of limited reactions across all surfaces, retention of water by adsorption on participating solids [24] and, on generation of a pressure of product H₂O, a contribution from the reverse reaction.

α-NiSO₄·6H₂O

From consideration of kinetic, microscopic and heat absorption measurements during dehydration of α-NiSO₄·6H₂O, Guarini concluded [25] that two types of behaviour controlled the reaction rate. The elimination of water vapour and the crystallization of product did not necessarily coincide. Below about 370 K the rate of product crystallization was comparable with the dehydration process, but at higher

temperatures the surface layer became impermeable [13, 26] leading to a deceleratory reaction.

$\text{Ca}(\text{OH})_2$

The original crystal structure was retained throughout much of the dehydroxylation of $\text{Ca}(\text{OH})_2$ [27]. Kinetic behaviour was interpreted [28] as water loss under diffusion control. The dehydrated material later recrystallized, apparently [28] by a nucleation and growth process, but the water elimination and product phase generation did not coincide in space.

Water elimination closely followed by recrystallization

$d\text{-LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$

The limited, deceleratory initial reaction during dehydration of $d\text{-LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ was identified [16] as the diffusive loss of water from an unrecrystallized surface layer that became more disordered as the concentration of water site vacancies increased. After this process, a textural change was detected, by microscopic observation, about $1 \mu\text{m}$ below the crystal face. Kinetic measurements led to the conclusion [16] that reactions at boundaries of nuclei, active in the main dehydration, proceeded at the same rate as the initial dehydration, but the anhydrous recrystallized product provided seed crystals which enable the transformation of dehydrated material to the product phase to continue. The presence of this solid facilitated the difficult step and opened channels permitting the escape of water essential for continued nucleus growth. The recrystallization zone, therefore, followed closely after the diffusive loss of water occurring within a zone of thickness of the order of $1 \mu\text{m}$ (based on the microscopically observed textural discontinuity that was identified beneath the outer faces of dehydrated crystal).

Explosive thermal dehydrations

Stoch [29] reviewed a number of reactions in which there was homogeneous and reversible intracrystalline dehydration to yield product H_2O molecules that remain trapped within the crystal structure. These reactants are effectively sealed containers and when the internal pressure exceeds the tensile strength of the weakest bonds of the container there is irreversible disintegration of the reactant particle. This dehydration mechanism involves no advancing interface and is, therefore, a separate class. Such behaviour has been described for the calcium borates: colemanite (at 648 K) and pandermite (at about 711 K) together with some layer silicates.

Mechanisms of dehydration of crystalline hydrates

The dehydration studies mentioned above provide ample evidence to support the conclusion that the chemical steps contributing to water elimination may occur within the reactant phase at zones that do not coincide with the interface at which

there is recrystallization of reactant to product (Fig. 4). Little information is yet available concerning the structures, properties and spatial relationships between the two zones in which there is (i) water elimination from the reactant structure and (ii) recrystallization perhaps accompanied by further water evolution. Some aspects of mechanisms of this type are discussed in the articles cited above. The only reaction in which a direct chemical interrelationship of the two steps is identified appears to be the dehydration of *d*-LiKC₄H₄O₆·H₂O [16].

The characterization of the kinetic contributions from two processes occurring at two interfaces is more difficult than interpretation by a single geometric model [1]. If the two steps remain in close proximity, it may be possible to treat the complex reaction zone as a single interface. This model may be acceptable for many dehydrations. When product recrystallization, however, appears as a distinct process, advancing as an interface in largely dehydrated material, a proper description of the overall reaction requires kinetic and geometric information about each of the contributing steps, e.g., the rate of H₂O evolution and estimates of the volumes of recrystallized product from the numbers and sizes of nuclei. Such observations, including their relative variations with time, may enable the individual roles of the two rate processes to be distinguished, at least semi-quantitatively. Thermochemical observations may also be used to establish kinetic controls, particularly with regard to initial surface contributions [8, 30].

Recognition that solid-state dehydrations may commence with the generation of a thin, modified surface zone must be accommodated in the formulation of reaction mechanisms. Nucleation, for example, may occur within the reacted surface material, beneath this modified material, or at the contact between these. Orientation relationships with the parent lattice may result (topotactic growth). Extensive surface metamorphism, including possible distortion of the boundary layer, provides an explanation of the difficulties in associating sites of onset of reaction with points of surface termination of dislocations [31–34]. Retention of water beneath an impervious surface barrier may promote the difficult step of product recrystallization [6, 7, 13]. Studies of growth have often been directed towards the difficult task of characterizing the chemical changes that occur in front of (or behind) the obvious textural discontinuity. Nucleus growth has been shown to be promoted by the presence of water vapour [6], condensed liquid product [12] and of seed crystals [16]. The mechanism may depend on reaction temperature [12], but clearly there is much still to be learned about interface chemistry and rate controls.

Decompositions of solids

We are aware of no observations of textural modifications that are comparable with "orange peel" development for reactions other than dehydrations. For example, decomposition of CaCO₃(→CaO+CO₂) is a nucleation and growth process [1, 31]. The original surfaces, exposed by cleavage, undergo relatively little retexturing apart from cracking due to product shrinkage (Fig. 5). At this early stage, relatively few cracks are evident in each nucleus, apparently the product is not finely divided and retains contact with the reactant.

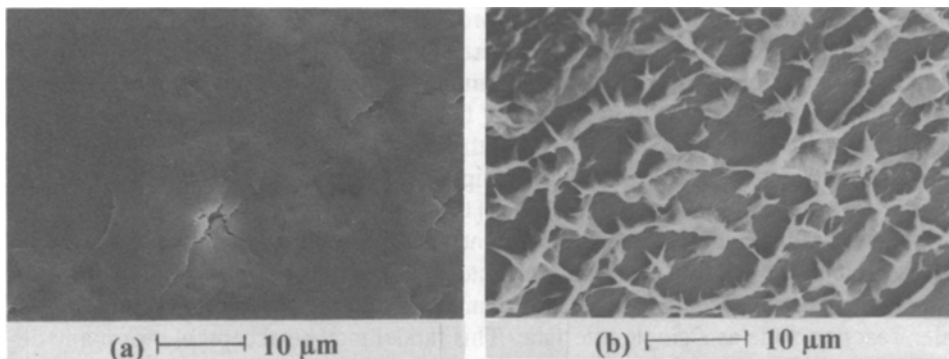


Fig. 5 Decomposition of CaCO_3 is a nucleation and growth process [1, 31]. The original surfaces, exposed by cleavage, undergo relatively little retexturing (a), apart from cracking, due to product shrinkage, evident in this replica (b) of an assemblage of nuclei (depth about $5\ \mu\text{m}$)

There is ample evidence, however, that identifiable, unreactive surface 'skins' appear during many solid-state decompositions, e.g., the decomposition of copper(II) malonate [15] (skin formed during the initial 3 to 5% reaction), the decompositions of alkali permanganates [17–19] and in the phase transformations of MClO_4 (where M is K, Rb or Cs) [35]. Whether these surface changes are the result of an initial rate process on heating, or result from deterioration during storage, requires further investigation. Furthermore their role in decompositions remains to be clarified. In an early study of nucleation during the decomposition of silver azide, Sawkill [36] showed that two forms of silver were produced. Randomly oriented silver separated at boundaries of a sub-structure of the crystal, whereas highly oriented silver existed as discrete nuclei. The nuclei were identified as regions into which silver diffuses to build up a fcc lattice having a spacing larger than that of normal silver metal and based on the silver ion positions in silver azide. Later this structure collapses to form the normal silver structure. Sizes of nuclei do not appear to change but their densities increase.

Conclusions

The articles cited above show that dehydrations of many crystalline hydrates are only approximately represented by the widely accepted reaction model of chemical change being completed within a thin reaction interface. The evidence presented distinguishes two steps in these reactions: water elimination and product crystallization, that do not necessarily coincide and whose spatial separation, particularly for water elimination, may be significant. Detection and characterization of these complementary processes require more sophisticated experimental techniques than have usually been employed, but are essential if understanding of these reactions is to be advanced. The role of surfaces in initiating reaction also requires further clarification. Investigations of solid-state dehydrations are identified as meriting

further effort in developing the theory of solid-state kinetics by increasing insights into reaction controls, interface chemistry and reaction mechanisms. As in the past [1] dehydrations are valuable model rate processes.

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