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SOLID-STATE DECOMPOSITIONS – STAGNATION OR PROGRESS?

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Abstract

An appraisal of the trends discerned in the recent literature concerned with solid-state decompositions suggests that this research area lacks a general theoretical framework and, hence, order in the subject is difficult to recognize. There have been surprisingly few reviews of the field. Many of the continuing flow of research publications may be of individual value, but most do not contribute to the overall development of the topic. For example, in many studies of reversible dissociations the sensitivity of rate characteristics to prevailing conditions is not discussed so that the fit of data to rate equations and the magnitudes of calculated Arrhenius parameters may be of empirical value only. Some studies report kinetic results without mechanistic discussions supported by complementary observations. Progress forward from an apparent state of stagnation depends upon more critical examination of the existing literature, coupled with better designed experiments to establish the reproducibility and reliability of kinetic conclusions. Techniques capable of providing insights into the bond redistribution steps that occur during reactions in crystals are also urgently needed.

Keywords: Arrhenius parameters, crystolysis, decomposition of solids, isothermal kinetics, non-isothermal kinetics, reaction mechanisms

Introduction

Reasons for studying the thermal decompositions of solids (crystolysis [1]) may range from the very practical to the very theoretical. An example of the practical extreme would be a study of the thermal stability of a specific solid substance under a set of conditions closely related to a technological process in which the substance is to be used. There may not be the time, funding and (even) the interest to explore more than a limited range of relevant conditions. In contrast, the detailed study of the thermal behaviour of a large number of different kinds of solid reactants under a variety of conditions has the ultimate (but not necessarily attainable) goal of evolving a theory of thermal stability of solids (TTSS). The present paper is principally concerned with identifying and discussing problems in developing and applying such a theory.

In these times of limited funding and resources for research, it is a valuable exercise to attempt to take stock of a subject which has been under investigation for a long time. It is now more than forty years since the publication of 'Chemistry of the Solid-state', edited by Garner [2], with contributed chapters from many authors who

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were, or became, leaders in the field. Extensive reviewing of the recent literature, leads us to the opinion that there is evidence of stagnation in the field. This view is based on the following generalizations.

(i) The subject area lacks coherence and the absence of a comprehensive theory means that reactions tend to be discussed individually. There are very few critical reviews of the numerous published studies and few attempts have been made to set up theoretical frameworks of general applicability.

(ii) Many reported kinetic studies are only of empirical value, because of the lack of allowance for the sensitivity of rate data to experimental conditions. Hence many reported kinetic observations, including activation parameters, are difficult to relate to any basic chemical or physical steps.

(iii) There has been an overemphasis, or even preoccupation, with the mathematical aspects of kinetic analysis, which has detracted from the effort needed to determine the physical and chemical significances of the measurements made.

(iv) The main experimental techniques available for studying the decompositions of solids are limited in the fundamental information that they are capable of providing and few new techniques have been developed.

These not unrelated criticisms are considered in more detail in the sections that follow.

The absence of a comprehensive theory

Theories of kinetics

In a fascinating survey of the history of Chemical Kinetics, Laidler [3] points out that chemical kinetics was essentially an empirical subject until about 1900, after which the ideas of thermodynamics, the kinetic theory of gases and of molecular statistics began to be combined to explain elementary reactions. The development of the transition-state theory around 1935 by Eyring, Polanyi and Evans provided a considerable improvement on collision theory and a valuable framework for the understanding of a wide range of types of chemical and physical processes and has led to qualitative insights into such features of homogeneous reactions as solvent effects, isotope effects and pressure influences. The history of the development of theories for unimolecular gas reactions [3] is also of great interest (and of relevance to crystolysis), because the dependence of the rate equation upon homogeneous reaction conditions was overlooked for a considerable time until careful experimentation by Lindemann, Christiansen and Hinshelwood and later contributions by Rice, Ramsperger, Kassel and Marcus.

Rate equations

The rate of product formation during decompositions of many solids is controlled by the advance into unchanged reactant of a reactant-product interface within which the chemical transformations occur. The changes with time of the geometry of this advancing interface determine the rate equation for reaction. A limited set of such geometric models, based on definition of the fractional extent of decomposition, α, in terms of a measurable quantity, for example the mass loss for an identified reaction (or reaction step), has been developed [4, 5]. These models lead to rate equations of the form:

$$\text{rate} \propto f(\alpha) \text{ or } g(\alpha)=kt$$

where $f(\alpha)$ and $g(\alpha)$ are conversion functions.

Garn [6] has challenged the validity of such representations on the grounds that reaction, localized at an interface, can hardly be significantly influenced by material remote from that interface. On the other hand, unless there is unreacted material, reaction will cease. It is easier to accept that:

$$\text{rate} \propto \text{number of reactant species in a `reaction situation' (RS)}$$

An RS may be regarded as analogous to the activated complex of homogeneous kinetic theory, but it seems unlikely that all reaction situations during the decomposition of a particular solid substance would be similar. On the interface advance model, the reaction of an RS leads to the production of ‘daughter’ RS sites. If the number and/or the reactivity of RS sites increases, acceleratory behaviour results. Linear behaviour could result from constant numbers and reactivity, or increasing numbers of lower reactivity (or, in principle, decreasing numbers of increased reactivity). The rate of formation of new RS sites will be related to the amount of ‘contactable’ unreacted material, which will probably be approximately represented by the overall amount of unreacted material $(1-\alpha)$.

It is important to note that rates of nucleation are more sensitive to the numbers, locations and interactions of crystal imperfections than are the rates of subsequent growth of nuclei. Individual separate nuclei are observed to grow at approximately the same rate on a given crystal surface. The relatively small proportion of the overall reaction involved in the formation of nuclei thus exerts a considerable control on subsequent kinetic behaviour by defining the initial distribution of the reaction interface within the reactant particles. These interfaces may be regarded as large, complex imperfections which advance at constant rate through the reactant, being little influenced by more minor imperfections. Chemical change within this reaction zone is the preferred (low-energy) path and this path is characteristic of the particular reactant.

Representation of the controlling step in a solid decomposition as a vibration along the reaction coordinate of a transition-state complex emphasizes the similarity of such reactions with homogeneous kinetic theory (the Polanyi–Wigner model [4, 5]). However, in the absence of the identification of the nature and the concentrations of the precursors to product formation, this model remains speculative and does not contribute to greater understanding of the overall pattern of chemical changes.

Three complementary aspects of interface reactions in crystalline solids require continued reappraisal. The mechanism by which the first n atoms form an entity called a ‘nucleus’ [7, 8]. The geometry of the advance of the resulting interface, which usually has a dominant influence on the kinetics. The mechanism, that is steps such as bond redistribution and recrystallization by which reactant is transformed into product, and which is more difficult to investigate directly. This relatively complicated reaction model contrasts with the energetic interaction of moving species during homogeneous reactions.

Arrhenius parameters

The temperature dependences of rate constants measured for reactions of solids are often satisfactorily expressed by the Arrhenius equation but the interpretations of the derived Arrhenius parameters (activation energy, E_a, and pre-exponential factor, A) must be different to those developed from the theories of homogeneous reactions [9].

The accuracy of reported values of E_a and A is not always discussed, but often uncertainties may be about ±10%. Such estimates are essential, not only for indicating the experimental reproducibility, but also for calculating the uncertainties in predicted rates or lifetimes.

The stereochemical restraints imposed by the crystal structure, which, at least partially, immobilise reactants, products and any intermediates, would invalidate the assumption made in homogeneous kinetics that a single activated-state controls the rate of reaction. Concurrent and/or consecutive processes taking place in the reaction zone (possibly with the participation of crystal imperfections) will involve more than one type of energy barrier and cause the numbers and the natures of these transition-states to change considerably during the course of reaction. Under these circumstances Arrhenius parameters can be expected to vary with extent of decomposition. The fact that initial decomposition is localized at surfaces or, even more specifically, at certain surface sites, indicates that it is differences in the bonding configurations which lead to reaction. The consequences of initial reaction may then be either the replenishment of such favourable reaction situations, or their consumption prior to continued reaction at the next most favourable set of sites. The possibility of change of the E_a value (and, probably, reaction mechanism) with extent of reaction, α, and/or across the temperature interval of measurements should thus be considered.

Literally thousands [4, 5] of values of A and E_a for solid decompositions are now available in the literature and more continue to appear, without attempts to classify this massive data source for any chemical purpose. Reservations have been expressed [10] about the significance of correlations found for endothermic, reversible dissociations, where E_a values were close to the reaction enthalpy [2].

One area where patterns of A and E_a magnitudes have been described is when isokinetic behaviour [11, 12] has been found. This is an ironic situation because compensation behaviour can be explained by a sensitivity of reactions rates to experimental conditions for rate processes proceeding within a common temperature interval. Here E_a values are compound terms, incorporating contributions from reaction reversibility, inhomogeneity, etc. Such values are not obviously related to a rate limiting step or to a fundamental reactivity control. Compensation behaviour may also arise for mathematical reasons [13] giving rise to various false isokinetic relationships.

For a limited number of (irreversible) decompositions (e.g. those of $KMnO_4$, $RbMnO_4$ and $CsMnO_4$ [14, 15], of NH_4ClO_4 [4, 16] and related perchlorates [17], possibly also $Ba(N_3)_2$ and NiC_2O_4 [4]) different workers have reported comparable magnitudes of E_a. Such agreement is not always close but the kinetic characteristics of these reactions appear to be relatively insensitive to reaction conditions.

Reaction mechanisms

In solid-state kinetics the term reaction mechanism tends to be used ambiguously. The more conventional usage in homogeneous kinetics refers to the sequence of steps by which a reactant is transformed into product. There has, however, also been a tendency to use reaction mechanism as a synonym for ‘rate equation’. Such imprecision is understandable when one looks more closely at what is involved in describing the ‘steps’ by which the transformation from reactant to product takes place. Johnston [18] has discussed this process of resolving a complex (homogeneous) chemical reaction into contributing steps. The levels of resolution can extend beyond the first stage of determining the elementary chemical reactions which contribute to the complex reaction, to examining increasingly abstract processes such as collisions, energy transfers and molecular rearrangements (‘elementary chemical-physical reactions’) which, in turn, contribute in various combinations to the elementary chemical reactions. Further resolution to ‘elementary physical interactions’, could be followed by the ultimate, and generally unattainable, limit of abstraction which would be the time-dependent quantum mechanical treatment of the particles concerned.

In crystolysis reactions, the molecular rearrangements (using ‘molecule’ in its widest sense) which are the major (and relatively uniform) features of homogeneous reactions other than redox reactions, are far less accessible to study because they take place mainly at or near the reactant/product interface. The way in which the position and shape of this interface changes with time, the way in which chemical species (including impurities and crystal imperfections) move to and from the interface, and the structural changes which take place ahead of and behind the advancing interface all form part of the description of a reaction mechanism. These essential contributory steps often can only be inferred indirectly from what is observed.

Classification systems

In Garner’s book [2], decompositions were divided very broadly into either endothermic (and often reversible) or exothermic (and usually irreversible) reactions. Another possible approach, classification by chemical composition [4, 5] has been less useful in providing insights into patterns of behaviour than might have been expected. We are not aware of any attempt to classify reactions on the basis of the applicability of a common conversion function, $f(\alpha)$ or $g(\alpha)$.

The current classification systems consider mainly (i) the type of process which is rate controlling: nucleation, growth, interface advance, diffusion, heat transfer, etc.; and/or (ii) the chemical nature of the solid within which decomposition occurs.

Clearly the behaviour of organic polymers is expected to be very different from that of inorganic highly-ionic solids. However, it has also been found that quite different types of behaviour can be observed within a group of chemically closely-related substances, e.g. Group IIA (alkaline-earth) carbonates [4, 5].

As long ago as 1965, Boldyrev [19] proposed a classification scheme for the decompositions of ionic solids. Reactions were divided into two main groups, distinguished by whether or not the chemical bond cleavage step was accompanied by electron transfer. The first group (in which there was no electron transfer) was sub-divided according to whether the process was reversible or irreversible. The second group (oxidation-reduction reactions) was sub-divided according to the nature of the electron transfer step, whether this occurred between lattice constituents or resulted in the intervention of a radical species.

This approach provided an admirable foundation for a general classification of crystolysis reactions, being flexible, comprehensive in application and amenable to refinement, but has not been significantly adopted, modified or developed. Nor has it been significantly criticized. Other generalizations in the subject have similarly found little acceptance or favour from a majority of authors. For example, Acheson and Galwey [20] identified the activation step in the breakdown of a range of carboxylates as the rupture of a covalent bond between the carboxyl group and the metal. Later Boldyrev *et al.* [21] concluded that the first stage in the thermal decompositions of all oxalates is the rupture of the C–C bond in the anion. A variety of possible controlling steps have been proposed for reactions of this type ([4], p. 210). This problem remains unresolved and has not received the consideration it deserves.

Boldyrev has reviewed [22] the chemistry of topochemical reactions. Galwey [8, 23] has discussed the forms and functions of interfaces in solid-state decomposition. However, many published articles direct little (if any) attention to the chemical mechanisms of the reactions for which E_a values (etc.) are published, or attempt to place the findings in a broader context. There are the promising mathematical contributions by Korobov [24] which could be of value in the development of the theory of heterogeneous kinetics.

A theory of thermal stability

An acceptable theory, of any kind, should be able to explain a range of observations using fewer principles than there are observations. Presumably, as the number of observations increases the number of principles required may also need to be increased.

Both thermodynamic and kinetic aspects must form the foundation of any theory of thermal stability of solids (TTSS). Thermodynamics will determine the temperature ranges over which endothermic decompositions are feasible, because entropies of decomposition are invariably positive. It is thus to be expected that explanations of the observed differences in behaviour during exothermic decompositions will involve control by kinetic factors. Because decompositions generally occur under conditions far from equilibrium, with non-homogeneous distributions of reaction zones, predictions based on equilibrium thermodynamics should generally be replaced by treatments using irreversible thermodynamics.

L'vov's work [25] is based on the interesting proposal that decomposition involves an initial sublimation step. For ionic compounds this corresponds to the process on which the calculation of lattice energies is based:

$$AB(s) \rightarrow A^{n+}(g) + B^{n-}(g)$$

followed by condensation of the less-volatile products. Because sublimation is invariably endothermic, condensation would have to make a major contribution to the heat balance for a decomposition to be exothermic overall. L'vov [25] has applied his ideas with considerable success to the published results for several types and series of related solid decompositions and this novel approach is worthy of careful examination for some, but not all, decompositions.

If the thermal behaviour of each crystalline substance counts for as little as one observation, can a small number of principles be used to interpret this large amount of information? One of the parameters that is accepted as influencing thermal stability is crystal structure. Immediately this suggests a major problem. Each crystalline substance has a unique structure. Those substances classified as isomorphous have overall similarities in symmetry, but unique dimensions, and there is the possibility that a single substance can take up different crystal structures under different conditions, e.g. temperature, pressure, presence of impurities, etc. These structural and dimensional differences result in differences in lattice energies and other physical properties, such as thermal and electrical conductivities, etc.

Even for one substance, with one crystal structure (maintained across a range of conditions), each preparation or sample of the substance will have a unique set and distribution of imperfections of various kinds, so that, in practice, no two samples of a solid can ever be identical, although they may be similar. There are many indications, however, that deviations from the ideal structure have a greater influence on the thermal stability of a solid than the crystal structure itself, as shown by the differences in kinetic behaviour observed between single crystals and powdered samples of the same reactant. Traces of impurities can also influence thermal stability without changing the crystal structure.

When comparing thermal stabilities of crystalline substances, the behaviour of similar single crystals of different reactants, A, B and C, may show smaller variation than that found for the same reactant A (say) in sample forms 1, 2 ..., n. Such observations suggest that a matrix of factors, in weighted combination, controls the observed thermal stability [26]. Experimental variation of some of these factors, if such variations can be produced without changes in interrelated factors, may indicate whether the weighting factors are large or small. It appears extremely unlikely, however, that any single chemical step, analogous to the individual bond rupture or electron transfer steps proposed in homogeneous reaction mechanisms, can be unambiguously identified as rate controlling. Steps such as bond rupture or electron transfer in the solid-state or at a solid surface will be influenced, at least to some extent, by the environment in which the process occurs and this environment is likely to change both with location and with time. This connectivity of factors [27] prevents the properties of complex systems from being understood by subdividing the system and examining a part separately, i.e. no part of the system is representative of the system as a whole. The question of interest then might become: if the complex system is comprised of all the decompositions of all the solids possible, under a wide range of experimental conditions, can one usefully examine any subset of observations and use the correlations obtained to explain and/or make general predictions about the complex system? (This might be regarded as similar to making predictions about world weather from observation of the weather in one selected geographical area.)

Sensitivity to reaction conditions

For reversible solid-state decompositions both the rate equation providing the 'best fit' to measured yield-time data [2, 4, 5, 28] and the magnitudes of the Arrhenius parameters are often sensitive to reaction conditions [4, 5, 11]. Rates of product formation are often significantly influenced by the conditions prevailing within the reactant mass (crystal or powder), most notably the availability of the volatile product in a dissociation reaction, which may vary with pressure and compositions of other gases present, reactant mass, particle sizes, dispersion, etc. Inhomogeneities within the reactant assemblage may also affect overall kinetic behaviour [29] and gas diffusion may be an important controlling parameter.

Because reversible decompositions are usually endothermic, the possibility of self-cooling has also to be considered. The characteristic pattern of variation of the rate of dehydration of crystalline hydrates with increasing water-vapour pressure, known as the Smith–Topley effect [5], has been shown, in a computer simulation by L'vov *et al.* [30], to be explicable in terms of self-cooling, with the rate maximum being determined by the powder grain size.

In many published articles, describing rate studies for a novel reaction, the possibility of reversibility is not even mentioned and the sensitivity of rate data to variations in reaction conditions has not been investigated. It follows that, for such limited kinetic studies, the conclusions may be empirical observations, applicable only to the specific experimental conditions prevailing during these measurements.

Values of E_a for reversible decompositions, measured under conditions designed to eliminate contributions from the reverse process, differ significantly from data obtained where the back reaction contributes even to a small extent [29, 31, 32]. Even if one attempts to eliminate those kinetic analyses based on erroneous or dubious grounds, the apparent kinetics of $CaCO_3$ decomposition are very sensitive to the procedural variables [33], the amount of CO_2 present, even when small masses of reactant are used, gas flow, etc. [34], and under these different conditions isokinetic behaviour is observed [11]. The activation energy for the decomposition of $CaCO_3$ (205 kJ mol^{-1}) measured at very low pressures has been shown to be appreciably larger than the dissociation enthalpy [31].

The diversity of kinetic results for dissociations is also illustrated by observations for the dehydrations of $Li_2SO_4 \cdot H_2O$ [35] and of $Ca(OH)_2$ [36], each of which exhibits compensation behaviour. Flanagan *et al.* [29] reported E_a=130 kJ mol^{-1} for the dehydration of nickel oxalate dihydrate from results extrapolated to zero reactant mass to eliminate contributions from the back reaction. This is significantly larger than other previously reported values for this reaction and it was shown that even a small water vapour pressure markedly decreased the rate of this reaction. This sensitivity of rates of reversible reactions to prevailing conditions contrasts with the more reproducible kinetic behaviour of some irreversible decompositions (mentioned in 'Arrhenius parameters' above). Compensation trends are also found in published kinetic data for the decompositions of many coordination compounds, for example [37].

These studies demonstrate the necessity for careful design and experimentation if rates of the forward reaction only are to be measured for reversible dissociations. Surprisingly few careful investigations of this type are to be found in the literature. Kinetic measurements made using relatively large reactant samples, in the presence of an inert gaseous atmosphere that inhibits escape of a volatile reaction product may be only of empirical value. The apparent values of A and E_a may, however, be of use for comparative studies, or for estimations required in the design of manufacturing or chemical treatment processes, or for predicting stabilities of pharmaceutical products, etc.

The Arrhenius equation can be used to extrapolate rate estimations beyond the temperature interval used in the original measurements, provided that the possibilities of mechanism changes that would invalidate the predictions are considered [38]. Such uncertainties must be greater for reversible reactions.

The mathematical emphasis of kinetic analysis

The advantages of obtaining kinetic data through programmed heating of the reactant have been very widely recognized [4, 5, 13, 39]. Numerous papers concerned both with the theory of the subject and reporting studies of various and diverse reactions have appeared. This approach, that easily yields abundant results by experimental and computational techniques that have been largely automated, has developed into a topic that possesses a momentum of its own. Much attention in these studies has been directed towards the resolution of mathematical problems rather than in establishing the factors that control reaction rates, such as the influences of heat and mass transfer within the reactant mass, reaction reversibility, inhomogeneities within the reactant mass, etc. While a few studies (for $CaCO_3$, $Li_2SO_4 \cdot H_2O$, $Ca(OH)_2$, etc.) have shown variations of A and E_a with conditions, it is not evident how widespread and how large such effects are for other salts.

Initially, much attention was directed at approximate methods for evaluation of the temperature integral. More recent numerical techniques have made such approximations unnecessary [40] and more attention needs to be directed, instead, towards the accuracy of the measurements of sample temperature [41].

A further topic of discussion has been the minimum number of experiments necessary to provide reliable kinetic conclusions. Tests of the reproducibility of measured rates, an indispensable endorsement of data reliability, are sometimes omitted. Values of kinetic parameters are often reported to an unrealistic number of significant figures, without error estimation.

The kinetic parameters calculated from isothermal data are generally [42, 43] not very dependent upon the conversion function chosen, while the opposite is true for non-isothermal methods. Vyazovkin and Wight [44] have clearly established the value of isoconversional methods of kinetic analysis in detecting the complex reaction mechanisms operating in the majority of reactions involving solids.

Many studies (isothermal or non-isothermal) are unjustifiably regarded as complete when the statistically most applicable rate equation has been identified and the apparent Arrhenius parameters have been calculated. Microscopic examinations, capable of confirming geometric conclusions, and the use of other complementary techniques to characterize the participating chemical processes, intermediates, structures, textures (etc.) are not always attempted. Many reports do not mention the possibility of melting during reaction, which may influence both the rate measurements and their interpretation [45].

Experimental techniques

Very rarely, if ever, in heterogeneous kinetics will the process that is accessible to experimental measurement be an ‘elementary chemical reaction’. Cooperative interactions are more probable. At best one could hope for a rate-determining process, clearly distinguished from all other more rapid sequences.

Hot-stage microscopy continues to provide useful geometrical information as well as phase identification. There is a need for development of reaction chambers for scanning electron microscopy so that observations are not restricted to high vacuum and ambient temperature conditions. Atomic force microscopy shows promise as a technique for providing insights into retexturing of surfaces.

Techniques have been suggested for probing the chemical steps at the reaction interface more directly, but most, in principle, are likely to introduce further uncertainties by interfering in the normal processes. For example, wet chemical analysis of reaction intermediates in a crystolysis reaction involves assumptions that solvents and reagents used can reach the reaction interface and remove the species of interest without producing other effects. Even the less molecularly invasive spectroscopic techniques depend on producing and measuring some response in the active species and the spectral excitation, as in homogeneous reactions, will generally change the normal course of reaction. Vyazovkin and Linert [13, 46] have indicated ways in which spectral data may be applied to support kinetic observations in identifying the rate limiting step [9]. This particular work was not concerned with a crystal decomposition but future development may extend work in this direction.

Examination of the evolved gaseous products of decomposition, using a sensitive analytical technique such as mass spectroscopy or Fourier transform infrared spectroscopy, has been relatively neglected [47]. The high temperature volatilization studies by L'vov [25] may be capable of providing insights into the mechanisms and controls of solid-state decompositions.

Conclusions

Future directions

Predictions of directions for profitable future development need to build on the strengths and achievements of the subject and to avoid or overcome the weaknesses identified. A major shortcoming is the lack of recent development or application of new experimental techniques which can give more direct chemical information about the processes occurring within a relatively inaccessible reaction zone, possibly of molecular dimensions. An ideal probe capable of providing such information would have to operate at the reaction temperature without significant interference in the reaction processes, but have high spatial and time resolutions. The most promising, but not generally accessible, technique has been diffraction studies using synchrotron radiation [48].

Those model reactions that have contributed to the advance of the subject will, no doubt, be re-examined in the future. No reactant need be excluded from examination on the grounds that it has been investigated previously, provided that novel aspects of the reaction are addressed, or new experimental techniques are applied. Progress through persistence is covered in the thought-provoking review by Herbstein *et al.* [49] entitled 'Old and new studies of the thermal decomposition of potassium permanganate' and in a subsequent conference presentation [50] 'What almost two hundred years of research has taught us about the thermal decomposition of potassium permanganate.'

Progress does, however, require ever more precise and imaginative research. Investigation of any crystolysis reaction should include determination of the role (if any) of precursor changes (e.g., recrystallization and/or a previous reaction, such as dehydration, together with cracking or diffusive loss of constituents, or more subtle changes [51]). When an interface is visible, the dominant process in this zone may be identifiable as recrystallization accompanied by a catalytic or strain-promoted chemical change. Reaction and recrystallization are not, however, necessarily completed within the same advancing zones and may not always occur concurrently [52].

Retention of crystallographic structural features (topotaxy) or loss of local order (melting) must also be investigated. Changes which may occur behind the reaction front include secondary reactions between primary products, volatile product retention (including reversible rate processes) and retexturing of the residual solid.

Of all types of crystolysis reactions, understanding of dehydrations now appears to be most advanced and it remains to be seen whether the mechanistic patterns of behaviour recently proposed [5] are of wider applicability. Systematic comparisons of the thermal behaviour of other groups of related solid coordination compounds could yield results of value in developing a theoretical framework. Much also remains to be established concerning the chemical steps in nucleation processes and structures of reaction interfaces.

Parallels with heterogeneous catalysis

In attempting to identify the parameters that control decompositions of solids, including interface reactions, it is worth exploring the possibilities that parallels exist with the theory of heterogeneous catalytic reactions. For both groups of reactions the controlling step might either be the breakdown of an immobilized surface species or reaction by a range of two-dimensional analogues of homogeneous behaviour involving interactions between mobile adsorbed participants. These models have been discussed by Shannon [53] and by Cordes [54]. Again quantitative information concerning the identities of the precursors to product formation and their concentrations tends to be lacking. The proportion of the surface that is active is also not known.

One approach to increasing our understanding of the mechanisms of heterogeneous catalytic reactions has been to measure reaction rates for exceptionally well-defined systems. A selected crystallographic face of an almost perfect crystal of the active solid is exposed to very low concentrations of reactant gases for which surface occupancies can be measured and the rate of product formation determined. Low temperature (slow) experiments of this type undoubtedly provide insights into surface catalytic properties. Results, however, cannot be reliably extrapolated to higher temperatures and saturation surface coverage where the character of the reaction and the properties of material retained at the surface may be quite different. This modification may extend to surface retexturing [55] where atoms from the active solid appear to migrate while existing as surface intermediates. This latter situation, saturation coverage of the active surface accompanied by continual retexturing as the crystal undergoes chemical change, is an indispensable feature of most crystolysis reactions. Thus, patterns of mechanistic behaviour based on model heterogeneous reactions are unlikely to be applicable. Much less is known about the controls that apply when surface catalysis is most active, behaviour with which most crystolysis reactions should be compared. In the presence of two (or more) crystallographic phases (together with concurrent retexturing), it will be even more difficult to identify the factors controlling reaction rates.

Further work required

In the absence of a model that represents chemical changes at interfaces, the following features of such reactions require consideration and further investigation could be expected to advance the subject.

(i) Surface reactions. A full description of the rate of product formation requires measurements of the concentrations of all active participants and the surface area of the particular crystallographic faces (or other locations) across which these changes occur. This information is not usually available because of the lack of techniques to characterize and measure concentrations of the participating species. One approach may be through the use of spectroscopic methods to determine interface impurity levels [9] where energy levels or bands may be correlated with E_a values.

(ii) The structure of the interface. Where the residual solid retains crystallographic characteristics of the reactant (topotactic reactions), the decomposition may

be controlled by a diffusion step through which a reactant constituent is expelled from the ordered structure. Where there is little, if any, structural relationship between reactant and solid product, chemical processes may be influenced by the strain developed within the regions of contact between the reactant and product crystals. Little is known about the chemistry of interface reactions.

(iii) Alternative reaction mechanisms. Reactions at interfaces may include types of behaviour that are generally regarded as ineffective in homogeneous processes. Immobilized absorbed species concentrated at a saturated surface can be regarded as subject to an extreme form of a ‘cage’ effect. Repetitive collisions with neighbours may possibly lead to reactions of high ‘molecularity’. Sequences of chemical changes involving reactive intermediates can be envisaged where participants are retained (at locally relatively high concentrations) within the reaction zone. There is also the possibility of alternative mechanisms, such as the intervention of melting [45], which may be localized and temporary.

*(iv) Nucleation and growth reaction*s. While the nucleation and growth reaction [2, 4, 5] model is an accepted pattern of behaviour, reasons for the preferential occurrence of reaction below the reactant surface require investigation because the escape of volatile product would be expected to proceed most readily from outer reactant faces. It is, therefore, not obvious why reactions should occur at an advancing front composed of reactant and solid product while outer surfaces remain apparently unchanged. The assumption that many reactions commence at a surface imperfection and proceed thereafter within a strained zone of reactant/product phase mismatch needs confirming and, possibly, refining.

Researches on the dehydrations of alums have provided an alternative explanation of nucleation and growth reactions [56, 57]. The reactivity of surfaces is diminished by partial loss of water on exposure to dehydration conditions. Reaction ceases due to the inability of the material to recrystallize, which, however, is possible at a limited number of nucleation sites. Recrystallization, enabling reaction to continue within each nucleus, is facilitated by the temporarily retained water. The nucleus is, therefore, a structure for the temporary retention of volatile product. This would also explain autocatalysis. The properties of surfaces during dehydrations have been described for a range of crystalline hydrates [58–60]. In a quite different nucleation and growth reaction ($KBr+\frac{1}{2}Cl_2 \rightarrow KCl+\frac{1}{2}Br_2$) there was evidence that the chemical change proceeded in an intranuclear liquid phase [61].

Comment

The formulating of chemical mechanisms for reactions of solids has turned out to be far more difficult than was foreseen in early work. The information available about crystolysis reactions seems to form no coherent pattern and there are no criteria for the classification of reactivities of solid reactants. There is also no accepted basis for predicting the thermal behaviour of a hitherto untested solid reactant. Without some sort of theoretical framework, the value of data already collected is difficult to assess and comparisons with other branches of chemistry are difficult to make.

Imaginative, innovative and more critical generalized research, which seeks correlations within the subject, is required to overcome this perceived stagnation. There is a need for systematic reviews of the extensive material already published with attempts to develop or apply systems of classification. New experimental techniques capable of giving information about structures, textures, compositions, properties, etc. of reaction zones, are also needed. Considerable practical and theoretical rewards await those contributing to the future development of this important subject.

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References

1 N. J. Carr and A. K. Galwey, Thermochim. Acta, 79 (1984) 323.
2 W. E. Garner, Chemistry of the Solid State, Butterworths, London 1955.
3 K. J. Laidler, The World of Physical Chemistry, Oxford University Press, Oxford, 1993, Chap. 8.
4 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State, Comprehensive Chemical Kinetics, (Eds C. H. Bamford and C. F. H. Tipper), Vol. 22, Elsevier, Amsterdam 1980.
5 A. K. Galwey and M. E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam 1999.
6 P. D. Garn, Thermochim. Acta, 135 (1988) 71.
7 A. K. Galwey and G. M. Laverty, Solid State Ionics, 38 (1990) 155.
8 A. K. Galwey, React. Solids, 8 (1990) 211.
9 A. K. Galwey and M. E. Brown, Proc. R. Soc. London, A450 (1995) 501.
10 A. K. Galwey, Thermochim. Acta, 242 (1994) 259.
11 A. K. Galwey and M. E. Brown, Thermochim. Acta, 300 (1997) 107.
12 A. K. Galwey, Thermochim. Acta, 294 (1997) 205.
13 S. Vyazovkin and W. Linert, Int. Rev. Phys. Chem., 14 (1995) 335.
14 M. E. Brown, A. K. Galwey, M. A. Mohamed and H. Tanaka, Thermochim. Acta, 235 (1994) 255.
15 A. K. Galwey, S. A. Lyle and S. A. A. Mansour, Thermochim. Acta, 235 (1994) 239.
16 P. W. M. Jacobs and H. M. Whitehead, Chem. Rev., 69 (1969) 551.
17 A. K. Galwey and M. A. Mohamed, Proc. R. Soc. London, A396 (1984) 425.
18 H. S. Johnston, Gas Phase Reaction Rate Theory, Ronald Press, New York, 1966, Chap. 1.
19 V. V. Boldyrev, Kinet. Katal., 6 (1965) 934.
20 R. J. Acheson and A. K. Galwey, J. Chem. Soc. A, (1967) 1167.
21 V. V. Boldyrev, I. S. Nev'yantsev, Yu. I. Mikhailov and E. F. Khairetdinov, Kinet. Katal., 11 (1970) 367.
22 V. V. Boldyrev, J. Thermal Anal., 7 (1975) 685; 8 (1975) 175.
23 A. K. Galwey, Thermochim. Acta, 96 (1985) 259.
24 A. Korobov, Thermochim. Acta, 254 (1995) 1; 243 (1994) 79.
25 B. V. L'vov, Spectrochim. Acta, B 52 (1997) 1; B 53 (1998) 809; Thermochim. Acta, 291 (1997) 179; 303 (1997) 161; 315 (1998) 145; B. V. L'vov and A. V. Novichikhin,

Spectrochim. Acta, B 50 (1995) 1427, 1459; Thermochim. Acta, 290 (1997) 239; B. V. L'vov, A. V. Novichikhin and A. O. Dyakov, Thermochim. Acta, 315 (1998) 135.
26 M. E. Brown and R. E. Brown, Thermochim. Acta, (2000) in press.
27 J. L. Casti, Complexification, Abacus, London 1994.
28 A. K. Galwey and M. E. Brown, Thermochim. Acta, 269/270 (1995) 1.
29 T. B. Flanagan, J. W. Simons and P. M. Fichte, Chem. Commun., (1971) 370.
30 B. V. L'vov, A. V. Novichikhin and A. O. Dyakov, Thermochim. Acta, 315 (1998) 169.
31 D. Beruto and A. W. Searcy, J. Chem. Soc., Faraday Trans. I, 70 (1974) 2145.
32 T. Darroudl and A. W. Searcy, J. Phys. Chem., 85 (1981) 3971.
33 F. W. Wilburn, J. H. Sharp, D. M. Tinsley and R. M. McIntosh, J. Thermal Anal., 37 (1991) 2003, 2021.
34 P. K. Gallagher and D. W. Johnson, Thermochim. Acta, 14 (1976) 255.
35 M. E. Brown, A. K. Galwey and A. Li Wan Po, Thermochim. Acta, 203 (1992) 221; 220 (1993) 131.
36 A. K. Galwey and G. M. Laverty, Thermochim. Acta, 228 (1993) 359.
37 P. Mu, R-F. Wang and L. Zhao, Thermochim. Acta, 296 (1997) 129.
38 J. H. Flynn, J. Thermal Anal., 44 (1995) 499.
39 A. K. Galwey and M. E. Brown, Handbook of Thermal Analysis and Calorimetry, Vol. 1, (Ed. M. E. Brown), Elsevier, Amsterdam 1998, Chap. 3.
40 J. H. Flynn, Thermochim. Acta, 300 (1997) 83.
41 M. E. Brown, T. T. Bhengu and D. K. Sanyal, Thermochim. Acta, 244 (1994) 141.
42 J. M. Criado, M. Gonzalez and C. Real, J. Thermal Anal., 29 (1984) 243.
43 S. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 35 (1989) 2169.
44 S. Vyazovkin and C. A. Wight, Ann. Rev. Phys. Chem., 48 (1997) 125; Int. Rev. Phys. Chem., 17 (1998) 407.
45 A. K. Galwey, Thermochim. Acta, 269/270 (1995) 621; Pure Appl. Chem., 67 (1995) 1809.
46 S. Vyazovkin and W. Linert, Thermochim. Acta, 269/270 (1995) 61.
47 E. Kaiserberger and E. Post, Thermochim. Acta, 295 (1997) 73.
48 V. V. Boldyrev, Y. A. Gapanov, N. Z. Lyakhov, A. A. Politov, B. P. Tolochko, T. P. Shakhtshneider and M. A. Sheromov, Nucl. Inst. Method. Phys. Res., A261 (1987) 192.
49 F. H. Herbstein, M. Kapon and A. Weissman, J. Thermal Anal., 41 (1994) 303.
50 F. H. Herbstein, Proc. Israel–Hungary Binational Conference on Thermal Analysis and Calorimetry of Materials, Ein-Bokek, Israel, 1996, p. 6.
51 O. Chaix-Pluchery, J. C. Niepce and F. Freund, React. Solids, 8 (1990) 323.
52 G. G. T. Guarini, J. Thermal Anal., 41 (1994) 287.
53 R. D. Shannon, Trans. Faraday Soc., 60 (1964) 1902.
54 H. F. Cordes, J. Phys. Chem., 72 (1968) 2185.
55 A. K. Galwey, P. Gray, J. F. Griffiths and S. M. Hasko, Nature (London), 313 (1985) 668.
56 A. K. Galwey, R. Spinicci and G. G. T. Guarini, Proc. R. Soc. London, A378 (1981) 477.
57 A. K. Galwey and G. G. T. Guarini, Proc. R. Soc. London, A441 (1993) 313.
58 M. E. Brown, A. K. Galwey and G. G. T. Guarini, J. Thermal Anal., 49 (1997) 1135.
59 G. G. T. Guarini and L. Dei, J. Chem. Soc., Faraday Trans. I, 79 (1983) 1599.
60 G. G. T. Guarini and S. Piccini, J. Chem. Soc., Faraday Trans. I, 84 (1988) 331.
61 A. K. Galwey and L. Pöppl, Phil. Trans. R. Soc. London, A311 (1984) 159.