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Review Paper

WHAT CAN WE LEARN ABOUT THE MECHANISMS OF THERMAL DECOMPOSITIONS OF SOLIDS FROM KINETIC MEASUREMENTS?

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Aspects of the theories that are conventionally and widely used for the kinetic analyses of thermal decompositions of solids, crystolysis reactions, are discussed critically. Particular emphasis is placed on shortcomings which arise because reaction models, originally developed for simple homogeneous reactions, have been extended, without adequate justification, to represent heterogeneous breakdowns of crystalline reactants. A further difficulty in the mechanistic interpretation of kinetic data obtained for solid-state reactions is that these rate measurements are often influenced by secondary controls. These include: (*i*) variations of reactant properties (particle sizes, reactant imperfections, nucleation and growth steps, etc.), (*ii*) the effects of reaction reversibility, of self-cooling, etc. and (*iii*) complex reaction mechanisms (concurrent and/or consecutive reactions, melting, etc.). A consequence of the contributions from these secondary rate controls is that the magnitudes of many reported kinetic parameters are empirical and results of chemical significance are not necessarily obtained by the most frequently used methods of rate data interpretation. Insights into the chemistry, controls and mechanisms of solid-state decompositions, in general, require more detailed and more extensive kinetic observations than are usually made. The value of complementary investigations, including microscopy, diffraction, etc., in interpreting measured rate data is also emphasized.

Three different approaches to the formulation of theory generally applicable to crystolysis reactions are distinguished in the literature. These are: (*i*) acceptance that the concepts of homogeneous reaction kinetics are (approximately) applicable (assumed by many researchers), (*ii*) detailed examination of all experimentally accessible aspects of reaction chemistry, but with reduced emphasis on reaction kinetics (Boldyrev) and (*iii*) identification of rate control with a reactant vaporization step (L'vov). From the literature it appears that, while the foundations of the widely used model (*i*) remain unsatisfactory, the alternatives, (*ii*) and (*iii*), have not yet found favour. Currently, there appears to be no interest in, or discernible effort being directed towards, resolving this unsustainable situation in which three alternative theories remain available to account for the same phenomena. Surely, this is an unacceptable and unsustainable situation in a scientific discipline and requires urgent resolution?

Keywords: *crystolysis reactions, kinetics of reactions of solids, mechanisms of solid reactions, solid decompositions, thermal decompositions of solids*

Introduction

The theory of reaction kinetics, as routinely applied to thermal decompositions of solids, crystolysis reactions [1], uses scientific terms and concepts 'borrowed' from the theory of homogeneous reaction kinetics. Unfortunately, this loan is not based on substantial sureties or generally accepted conversion values. While kinetic terminology provides the wherewithall by which research capital may be deposited in The Literature Bank, the credit rating of some of these lodgements is dubious because the theoretical descriptive terms used lack the substantive guarantees of reliable, agreed definitions, the 'Gold Standard' for scientific discussion. Uncertainties in the precise meanings of essential terms, used when reporting thermal properties and when describing the behaviour of solids, devalues the systematic scientific development and theory of the subject. While a new and trustworthy currency for terminological exchange cannot yet be provided, some now devalued notes from the past can be recommended for withdrawal from circulation.

The objective of the present paper is to discuss particular shortcomings in the theories and assumptions that are routinely used to represent crystolysis reactions [1]. An appraisal is made of the theoretical significance of the concepts and interpretative methods that are conventionally, but often uncritically,

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used throughout the extensive literature concerned with thermal decompositions of crystalline reactants. Patterns of rate behaviour, described in recent publications as being characteristic of thermal reactions, are discussed: mechanistic interpretations of the observations obtained from studies of such decompositions are often analyzed and interpreted with the unstated, and unconfirmed, assumption that they take place in the solid-state. (This topic is often treated almost as a distinct discipline.) The present article also includes consideration of some problems of data evaluation and in the formulation of mechanisms for this type of rate process, through references to alternative theoretical approaches that have been proposed to model the chemistry of crystolysis reactions.

Theories of reaction kinetics**

The terms [activation energy (*E*), frequency factor (*A*) and rate equation *g* (concentration terms)=*kt*] (sometimes collectively referred to as the 'kinetic triad') are fundamental theoretical concepts that are accepted throughout reaction kinetics. Rates of homogeneous reactions are expressed in these terms so that measured data relating the progress of a rate process with time and with temperature can be quantitatively interpreted, by the underlying theory [2], to provide insights into the reaction mechanism. Throughout this article, 'reaction mechanism' describes the sequence of chemical steps through which reactants are transformed into products. These rate observations may also provide information about the factors controlling reactivity and the rate limiting process. Application of this approach to homogeneous gas reactions, first as collision theory and later, as developed into the more sophisticated transition state theory (TST), has steadily advanced our understanding of the steps participating in chemical changes and their controls. The same concepts and theory have been successfully extended to give insights into the rates of reactions in solution. These widespread successes of reaction kinetics have lead to the tacit acceptance of the view that (it is possible that) all chemical changes are rate determined by a dominant slow step of the type envisaged in the TST. A primary objective of the scientific method is to seek to extend systematic order and the generalization of the application of the powerful TST kinetic model to include reactions in solids is a manifestation of this aspiration. Thus, rate studies of crystolysis reactions have adopted, usually implicitly, the tried and trusted (at least, for simple homogeneous reactions) TST theory. This adoption does not, however, necessarily and adequately distinguish the fundamental differences in the nature of the reaction rate controls operating when freely moving gaseous molecules interact from those applicable within the dominant step identified as controlling the rate of a reaction occurring in, at or on a crystal surface. The present account considers some consequences of this distinction (without including a description of the TST, which is widely available in texts concerned with chemical kinetics).

Boldyrev [3–5] was probably the earliest researcher, interested in thermal reactions of solids, to appreciate inherent limitations in the ability of the kinetic approach to elucidate the mechanisms of crystolysis reactions. He has consistently maintained this viewpoint but his arguments, based on examples of alternative kinetic characteristics shown by different samples of the same reactant, have been widely neglected. The present paper includes a survey of those kinetic characteristics of solid-state reactions that introduce uncertainties into the mechanistic interpretation of an observed fit of rate measurements to a set of rate expressions based on simple geometric models [1] together (invariably) with the Arrhenius equation. The analysis given below provides reasons and explanations for some errors and inconsistencies that may be present in reaction models formulated through the conventional methods used to analyse thermokinetic data. To emphasise the important distinction that the theoretical significance of kinetic parameters obtained for reactions of solids may be different from those used in discussions of homogeneous reactions, we append the prefix '*S*' to the former. Thus, the terms of the kinetic triad for a particular thermal (solid-state) reaction are represented here by *SA*, *SE*, $Sg(\alpha)=kt$. This is an alternative symbolism from the usual literature convention in which Arrhenius parameters are described as 'apparent' but use of the conventional symbols (*A* and *E*) is maintained.

Despite considerable uncertainty in the fundamental theory, including the significances of the kinetic triad terms, papers in the literature continue to report, for 'novel' compounds, conclusions from kinetic analyses based on conventional computer programs that analyze (often) minimum quantities of measured data [6–9]. The resulting massive accumulation of kinetic data reported for thermal reactions of diverse solids, many of which are undoubtedly empirical, has not been classified to develop the subject as the organic growth of a systematic scientific discipline. Consequently, it is argued here that reexamination of the validity of the kinetic foundations of the subject are more likely to contribute to advancement of knowledge than the continued collection of further

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** Limitations in the theory of chemical kinetics, as conventionally used for analyses and interpretations of measured rates of heterogeneous reactions, are recognized: conceptual principles developed for homogeneous reaction models may not be applicable examples of unreconcilable (i.e., individually isolated) kinetic triads. These only extend the already overlong list of such idiosyncratic values.

The TST model envisages, in the reaction rate controlling step that follows an energetic encounter between freely moving reactant species, an unstable (transitory) association of molecular fragments that soon undergoes a bond redistribution step. This intermediate is believed to retain structural features of the reactant precursors, distributed so that the transitory bond minimizes the overall energy of the complex. It is further assumed that the transitory state is not perturbed by outside influences during its brief existence. For reactions in a gas, this allows the TST complex to be represented by a structural model, which contrasts with reactions proceeding in a solid where precursor species (must be presumed to) retain links with its coherent crystal structure by maintaining interactions with its neighbours. In addition, the energy distribution function in a solid differs from the Maxwell–Boltzmann behaviour characteristic of gases [10]. It cannot be assumed, therefore, without more evidence than is currently available, that the reaction situation in a solid can be approximated to that portrayed by the TST. In the gas phase, reactions are frequently represented as mono- or bimolecular processes but, for solids, the structures of transition complexes and events immediately preceding their formation are not known or readily characterized experimentally. The term ‘molecularity’ is not meaningfully applicable to the description of reactions proceeding in crystals: an unknown number of neighbouring species may interact with any assumed activated species during its lifetime. The usual observation, that measured rate data for crystolysis reactions satisfactorily fit the Arrhenius equation, is, therefore, consistent with but does not prove that reactions in solids involve an activated TST-type complex [10].

In a simple homogeneous reaction, the magnitude of E is identified with the energy barrier to a bond redistribution step in the transition complex and, therefore, refers to a single, specified rate process: the transformation of well-defined reactant(s) into identified product(s). The theory [2] provides a method for determining the frequency of formation of the unstable complex (A), the height of the energy barrier to its formation (E) and the ease with which an identified, particular chemical change occurs. This model cannot be directly applied to account quantitatively for rates of solid-state reactions for the following reasons (amongst others).

- The chemical change that occurs during the controlling step is not usually known in detail. There are uncertainties in the identities and the concentrations of the precursors that (may?) be activated to form a TST-type complex (but of uncharacterized structure) and also of the primary products.
- The role of energy distribution in activating chemical change is less certain [10].

Kinetic characteristics of crystolysis reactions may be determined by two or more controlling influences[***]

The theory applied to interpret the kinetics of homogeneous reactions was originally developed to explain the rate characteristics of a single step, well-defined and fully identified, chemical change [2]. This ideal situation is probably unachievable in kinetic studies of crystolysis reactions, though some parallels may be found for favourable systems by the use of suitably designed experimental methods. Observations obtained using precisely selected observational techniques are, however, rarely reported. For many published studies of crystolysis reactions, it is highly probable that two, or more, rate-determining factors have exerted significant controls on the overall rate characteristics described. Many of the kinetic triads reported in the literature for thermal reactions of solids are, therefore, empirical and refer to composite, consecutive and/or complex reactions proceeding under reaction conditions that are incompletely and/or inadequately described [6–9].

The present Section lists and discusses reaction conditions in which one (or more) parameter, active in controlling rate and complementary to the dominant chemical step, exerts a significant influence upon the measured rate of the overall chemical change. This analysis is necessarily qualitative because, although kinetic expressions incorporating each effect mentioned, or representing limiting situations, may be derived, some of these contributions to rate control may vary sensitively with small changes of experimental conditions. Identifying and establishing the role of each and every factor that can actively contribute in determining the overall rate of an observed rate process, and the extent of its participation, may require targeted observations, collected across a range of carefully selected, and systematically varied, reaction situations. Identifications of the precise influences of sample environment and the elucidation of every effect that is capable

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[***] It cannot be assumed that a single ‘rate controlling step’ determines the overall kinetic characteristics of a solid-state decomposition. Situations in which multiple factors influence rate behaviour are reviewed: these include contributions from more than a single chemical rate process, e.g., nucleation and growth and the effects of reaction reversibility, self-cooling, etc., which may vary with experimental conditions

of varying the rate of a chemical change occurring within a solid reactant are rarely reported. Deconvolution, to separate quantitatively the individual contributions from each participating rate control, may require extensive precise and complementary observations, supported by appropriately designed experiments using sufficiently sensitive techniques. For many reported kinetic studies, however, the descriptions of experimental methods are woefully incomplete. Consequently, the rate characteristics reported are conditions-dependent (though this is not usually mentioned) and are, therefore, empirical.

The headings given below distinguish and classify a range of significant rate-influencing reaction controls, which are known to contribute actively in determining the overall kinetic behaviour observed for the many crystolysis reactions wherein more than a single rate influencing factor participates. For such processes, therefore, the rate constants measured are composite parameters [11] and the (apparent) magnitudes of the terms of the kinetic triad may vary between different studies and samples of the same reactant. Moreover, prevailing conditions may change during the course of a single reaction, varying the relative influences of the significant participating rate controls. Generalization of kinetic characteristics is not possible: for any particular system of interest, it is (probably) more profitable to separate and to measure each contributory control individually, by suitably designed experiments. In the specific systems discussed below, one or more of the following general considerations may apply. The theory of kinetic analysis of crystolysis reactions is reviewed in [1].

- In any crystolysis reaction, more than one of the different types of rate influencing effects mentioned below may contribute and the significance (relative magnitude) of each control may vary with conditions and as the chemical change advances.
- Kinetic behaviour may vary, sometimes sensitively, with modification of the reaction environment, the experimental conditions within the reaction zone.
- The kinetic measurements made (mass change, yield of one, of several individual, or of all, products, etc.) may be incapable of identifying and characterizing quantitatively every primary and secondary reaction that participates.
- Under some conditions, particularly during rapid reactions, inhomogeneities (of temperature, pressures of gaseous product, etc.) may develop within the reactant phase or particle mixture so that local magnitudes will then differ from the nominal mean (measured) values. Such variations may change with time and/or location within the reactant mass and are important where overall rates are influenced by the diffusion of heat and/or mass.

Interface advance reactions in solids: kinetic complexities

Kinetic analysis of interface advance reactions in solids, identification of the kinetic model (rate equation, $Sg(\alpha)=kt$) that describes the behaviour observed, conventionally proceeds by comparisons of rate data with a range of possible geometric reaction models. The set of rate equations considered derives from the several possible alternative patterns of systematic variations of the rate with time, representing different shapes in progressive changes of the relative areas of active advancing interfaces that occur as reaction proceeds [1]. The 'best fit' found, within the set of equations compared, is then accepted as describing changes in the three-dimensional interface geometry that characterize the progress of reaction, though the detailed criteria used to make such distinctions are not always reported. In the models usually considered, initiation of reaction is defined as nucleation, which is the generation of a new active interfacial zone within which the chemical change occurs preferentially. Once established, the nucleus enters the growth phase of interface advance. However, neither the nucleation nor the growth processes can be assumed to be rate controlled by a simple, single chemical step, independent of contiguous influences, of the type envisaged in the TST model.

Nucleation

In many nucleation and growth process, the generation of an active reaction interface is achieved at only a very few sites across the reactant crystal surfaces and has, therefore, been associated with the points of emergent dislocations [1]. Here structural distortions may locally diminish the energy barrier and/or the stereochemical constraints to reaction; for example, the role of line dislocations in initiating calcite decomposition is discussed in [12–14]. However, establishment of active interfaces may be much more complicated than a simple or single chemical step. Boldyrev has investigated and discussed the role of mobile defects and crystal strain in initiating decomposition and in generating nuclei during the breakdown of silver oxalate [15] and the role of strain in ammonium perchlorate decomposition [16]. Microscopic observations of small nuclei, supported by X-ray crystallographic and other physiochemical measurements, provide strong evidence that nucleation is not simple but involves interactions of imperfections and local distortion of the reactant solid structure. A 'nucleation step' model may, therefore, be an oversimplification of the sequence of interlinked chemical changes that are required to initiate and to establish reaction in the breakdown of many solids. It may be possible to measure rate data from which (apparent) Arrhenius parameter values (*SA* and *SE* for nucleation) may be calculated. However, in the absence of supporting evidence, these magnitudes should not be identified with rate control through a specific bond rupture step or the participation of a particular TST structure.

Growth

The chemical steps controlling interface advance may similarly involve imperfection interaction, movements of all participating species, including defects, and of strain within reactant and/or product phases, if crystallization of the residual material takes place within the reactive zone of chemical change. (Reactant breakdown at an interface is not necessarily or immediately followed by contiguous product phase crystallization.) Again, to elucidate a reaction mechanism, the possibility of complex behaviour must be investigated in detail by appropriate complementary experimental techniques for each reactant of interest [15, 16]. The necessary supporting observations must be directed towards identifying all relevant aspects of the changes taking place, perhaps including microscopy to establish textures in and adjoining the interface, diffraction to determine the structures of all participating phases and crystal strain/distortion, physicochemical observations to characterize defects and their mobilities, etc. From such information, it may be possible to identify the dominant factors controlling rate, at least for simple reactions, and thus formulate a reaction mechanism. Again, while measurements of nucleus growth rates may be used to calculate Arrhenius parameters (*SA* and *SE*) for interface advance, these should always be regarded as potentially composite parameters and cannot, without experimental support, be identified with any simple, single reaction.

Comment

This brief historical survey of kinetic aspects of thermal changes undergone by initially solid reactants, studies originally undertaken to obtain mechanistic information, provides the background necessary for consideration (below) of the kinetic behaviour shown by reactions rate-controlled by more than a single parameter. An important feature of all the evidence available [1] is that the rates both of nucleation and of growth processes are almost invariably represented satisfactorily by the Arrhenius equation. This is also consistent with the energy distributions within the highest occupied levels in a crystal [10, 17], though the Maxwell–Boltzmann function is not applicable in solids. However, the fit of rate data to the Arrhenius equation alone is not a sufficient condition to confirm that the TST model [2] is applicable to solid-state reactions. Indeed, the available evidence shows that the chemistry of interfaces is much more complicated than can be represented by a theory developed from consideration of the redistribution of energy and bonding within isolated and unstable transitory ‘molecules’. However, examination of the literature shows that discussions of decompositions of solids have largely moved away from the consideration of the chemical properties of the reactants involved [6–9]. This is inexplicable, during a period when there have been considerable advances in microscopy, diffraction [18] and other techniques capable of providing direct information about the detailed courses of interface reactions and their controls. Amazingly, those experimental methods which are potentially most capable of providing insights into the course of chemical changes proceeding in solids have been widely ignored by a large majority of researchers. Kinetic studies have remained the preferred approach, despite the inherent limitations of this method for elucidating the individual steps that participate in the overall crystolysis reaction, as pointed out some time ago [3, 4]. Uncertainties in the experimental techniques currently being widely used to interpret thermokinetic data have been discussed more recently [6–9].

Practices widely tolerated in recently published literature reports of thermokinetic investigations include the omission of statements of assumptions underlying the methods used in rate data interpretation and the absence of robust questioning of the reliabilities of the kinetic conclusions reached. Of particular interest here is the almost invariable use of the conventional computational models that have been specifically developed for applications to decompositions of solids [1]. Aspects of the unsatisfactory nature of this approach have already been discussed [6–9]. Implicit in many of these reports is the (unstated) expectation that the reader will accept that the results have chemical significance, normally including one or more items of the kinetic triad. The several patterns of kinetic characteristics, presented below, show that, under experimental conditions frequently used, the rates of many, if not most, crystolysis reactions may be rate-determined by more than a single controlling factor. For these, the rate constants calculated are composite parameters [11]. Consequently, the magnitudes of *SA*, *SE* and the form of the kinetic model are empirical, subject to influences from the experimental conditions, the physical form of the (solid) reactant, imperfections implanted during preparation, subsequent damage from pretreatment, etc. Without additional, independent and reliable, evidence, the parameters of the kinetic triad cannot, therefore, be assumed to have fundamental chemical significance or applicability beyond the conditions of the experiments used to measure those reaction rates. These problems are mentioned here again because limitations [6–9] in kinetic analyses remain unaddressed and unappreciated by many workers in the field.

Interface advance reactions: multiple controls

An important factor in determining the shape of fractional reaction, α–time curves for isothermal interface advance (nucleation and growth) crystolysis reactions is the density of nuclei initially formed on reactant surfaces. For a reactant composed of single, or a few, large relatively perfect crystals, there may be an initial induction period. Later, if nucleation is 'difficult', (high *SE* and low *SA*) a small number of nuclei may appear, distributed across the outer reactant surfaces and this is characterized by a rate process showing a pronounced initial acceleratory phase in a sigmoid shaped yield-time kinetic model [1]. In contrast, where there is facile and dense early nucleation (low *SE* and high *SA*), a layer of product is rapidly established across all crystal faces soon after the start of reaction; the rate starts at, or close to, a maximum value and is deceleratory thereafter. The rates of such reactions fit the 'contracting prism' kinetic models [1]. The controlling parameters that remain unconsidered in many kinetic studies include the surface area/crystal size of the reactant and the distribution of damaged sites (where nucleation may readily occur) across these particles. Although the nucleation process itself represents a relatively very small contribution to α, the numbers and distribution of growth nuclei formed strongly influence the shape of the subsequent α–time curve and, therefore, the kinetic model, *Sg*(α)=*kt*. The following selected examples demonstrate that different samples of the same reactant may exhibit different kinetic characteristics: the kinetic model is not a fundamental property of the particular chemical compound studied [3, 4]. For the decomposition of a particular solid reactant, variations of kinetic behaviour can arise from changes of crystal shape, size, perfection/damage, etc. and/or from changes in experimental conditions used. The references cited have been selected to be representative: other examples can be found, many in the older literature.

Abrasion of the reactant surface with product can initiate dehydration

When studying the dehydrations of crystalline hydrates (e.g., $CuSO_4 \cdot 5H_2O$), it has been recommended [19] that reaction should be started by gently rubbing the surface of a large reactant crystal with the solid decomposition product to generate an initial interface parallel with the original outer face. The (presumably) constant, or slightly deceleratory, maximum reaction rate during the earliest stages is contrasted with the 'more usual' sigmoid shaped curve, obtained when small crystals are used, because these cannot be artificially nucleated across all outer crystal faces. Later work [20] has shown, however, that pretreatment can induce prolific nucleation of dehydration for some hydrates. For $KCr(SO_4)_2 \cdot 12H_2O$, dehydration interrupted by admission of water vapour, results in dense nucleation on subsequent reevacuation. It was also demonstrated that the early growth rates of individual nuclei may differ from values later achieved.

Thermal decomposition of ammonium perchlorate

Comparative kinetic studies of the low temperature thermal decomposition of NH_4ClO_4 (AP) were undertaken [21] for different reactant samples: large single crystals, crushed powder and powder compressed into coherent pellets. Kinetic studies of decompositions of the orthorhombic salt were completed between about 490 and 513 K (crystallographic transition to the cubic form). The reactions of single crystals were well expressed by the Avrami–Erofeev equation [1] and the exponent (*n*) diminished from 4 to 3 at α=0.2, ascribed to completion of the nucleation contribution. For reactions of powders and pellets: *n*=4 and 3, respectively, throughout most of reaction, attributable to a significant influence from nucleation in the former and early completion of nucleation in the latter. Apparent magnitudes of *SE* increased in the sequence single crystal, powder and pellet (approximately: 78, 103, 126 kJ mol^{-1}). Decompositions of the cubic form (above 513 K) fitted the same equation with *n*=2 for single crystal, powder and pellet but *SE* values showed smaller variations: 106, 104 and 125 kJ mol^{-1}, respectively. The data [p. 417 of 1] show well-defined compensation behaviour [11] from which the isokinetic temperature was calculated as 481 K. This is close to the intervals used in the kinetic studies, consistent with almost constant reactivity for the different reactants compared, despite the Arrhenius parameter variations [11, 22]. The evidence here is that, for AP, the magnitudes of both *SA* and *SE*, also *Sg*(α)=*kt*, vary significantly with different physical forms or samples of reactant.

Thermal decomposition of potassium permanganate

Kinetic studies of the decomposition of $KMnO_4$ have reported that rate data fit the Prout–Tompkins equation and the Avrami–Erofeev equation [1], though the differences are probably too small to allow unambiguous distinction to be made between these alternatives [23]. Support from microscopic observations has not resolved the ambiguities in providing an adequate kinetic description of (what now appears to be) a sequence of two overlapping consecutive reactions [23], but had originally been regarded as a simple (one step) process [24]. It has since been shown [25, 26], that anion breakdown involves the intervention of the intermediate (solid) $K_3(MnO_4)_2$. Consequently, (at least) two rate processes participate, each requiring individual kinetic investigation and description.

Dehydration of *d*-lithium potassium tartrate monohydrate

Following the initial (deceleratory) water loss from a thin superficial layer of reactant, subsequent dehydration is a nucleation and growth process that is subject to diffusive control, similar to the first reaction, but requiring intermittent product recrystallization [27, 28]. The relative contribution of the first (superficial) reaction increased with decrease of reactant particle diameter for a range of sample sizes, obtained by sieving powder. The pattern of kinetic behaviour for dehydrations of reactants in the forms of crystal, powder and pellet varied significantly. There was also evidence that contact with crystalline dehydrated product substantially diminished the induction period to the second (nucleation and growth) rate process. The relatively slower reaction rates measured for dehydrations above 450 K were associated with (at least partial) melting. Reasons for this relatively complicated pattern of kinetic behaviour are discussed in [27, 28].

Thermal decomposition of irradiated silver malonate

Decomposition of unirradiated salt showed sigmoid shaped α–time curves, with *n*=2 (also 3), attributed to asymmetric growth of nuclei (Ag/C) in the lath shaped reactant crystallites [29]. Quantitative comparative studies [30] of decomposition rates for γ-preirradiated salt, after doses between 0 and $1.0 \cdot 10^9$ rad, showed that the shapes of α–time curves were not detectably changed, though the reaction rates increased significantly and systematically with dose. The *SE* value determined for salt after $7.5 \cdot 10^7$ rad agreed well with that for unirradiated salt (about 170 kJ mol^{-1}). It was concluded [29, 30] that decomposition proceeded through catalytic-type breakdown of the malonate anion on nucleus/product Ag metal surfaces. Promotion of reaction by irradiation was ascribed to the generation of additional sites for nucleation (effectively increasing *SA*).

Variations of reactivity between individual samples

Aspects of this topic have been discussed by Brown and Brown [31].

Interface advance reactions: reversibility

In early kinetic studies of reversible, endothermic dissociation reactions, it was noted that some values of *SE* were close to the magnitude of the enthalpy of the chemical change occurring, although there were significant exceptions [19]. This correlation has since been ascribed to reactant equilibration between gaseous and residual products within the (reacted) outer layers of the original particles [32, 33]. Under high vacuum conditions, the contribution from the reverse reaction (that yielding reactant) can be diminished and the *SE* value increases above that of the dissociation enthalpy [32]. Variations of the (so-called) procedural variables [34, 35] (sample size, particle size, heating rate, pressure of gaseous product, etc.) often result in significant changes of the magnitudes of *SA* and of *SE*. Calcite dissociation, in particular, exhibits considerable (even extraordinary) ranges of extreme values, which exhibit compensation effects [36, 37]. Reasons for this behaviour have been discussed in Section 4.3 of [38], also [11], and need not be repeated here, except to emphasize that during some faster reactions the apparent rate characteristics (*SA* and *SE*) become particularly sensitive to experimental conditions. Kinetic behaviour changes at higher heating rates, in the presence of larger pressures of CO_2, etc., and when diffusion of heat and/or product gases probably result in the development of local inhomogeneities within the reactant mass, powder or larger particles. While calcite dissociation has attracted particular interest, featuring amongst 'the most intensively studied solid reactants', other substances exhibit similar trends, including magnesium carbonate [34, 35] and the dehydration of nickel oxalate dihydrate [39].

For reactions of this type, it may be possible to measure the rate of the chemically controlling interface dissociation step, under experimental conditions designed to remove rapidly the volatilized product from the reaction zone [32, 33, 39]. However, in the absence of a demonstration that this condition has been achieved, contributions from the reverse step, wherein the product participates in the establishment of dissociation equilibrium, probably exert greater or lesser control on the overall, measured reaction rate. Consequently, the empirical rate constants found are condition-dependent, and do not provide information about the kinetics of any proposed, and assumed dominant, rate-determining interface step.

Interface advance reactions: self-cooling/self-heating

The enthalpy changes that occur during endothermic rate processes (dehydrations, carbonate dissociations, etc.) can be sufficiently large to cause significant cooling within the active zone of the reaction interface.

This was recognized during early studies and due allowances were made when calculating Arrhenius parameters [19]. The need to include these temperature corrections, larger at higher reaction rates, became forgotten in subsequent researches and was routinely ignored until its importance was demonstrated by Bertrand and coworkers in 1974 [40, 41] to explain the Smith–Topley effect [1]. However, as was pointed out more than two decades later (1998) by L'vov and colleagues [42], 'they did not receive as much recognition'. In this paper [42], a theoretical method for estimating the influence of self-cooling was presented and quantitatively applied to the dehydration of $Li_2SO_4 \cdot H_2O$. L'vov later reviewed [43] and extended this model to calculate temperature distributions during decompositions of several carbonates. His conclusions included the observations that self-cooling is 'of primary importance in the explanation of…the kinetics of carbonate decomposition' and it is a reason for 'underestimation of the E parameters'. For the many kinetic studies that do not include appropriate allowance for interface temperature deviations, due to reactant self-cooling (or -heating), measured magnitudes of the Arrhenius parameters may be appreciably in error.

Complicated reactions: concurrent rate processes, melting, etc.

The occurrence of two (or more) concurrent rate processes, each involving an individual rate-determining step (including, for example, the overlap of consecutive reactions, complex mechanisms of thermal reactions, the involvement of several steps and/or melting, etc.), results in complicated kinetic behaviour. For such systems, the complete elucidation of kinetic characteristics and mechanisms may require the design of specific experiments to separate, to measure and to analyse kinetically, the individual contributions from each of the participating rate process. In addition, the overall kinetic behaviour may further be influenced by any, or by all, of the effects mentioned above (reversibility, self-cooling/heating, etc.) Some examples of diverse decompositions, which exhibit complex kinetic behaviour, are listed below.

Concurrent or overlapping consecutive reactions

Any complicated reaction, which includes concurrent contributions from two or more distinct and different rate processes, will yield composite *SA* and *SE* values that are not necessarily representative of either component reaction and are themselves, of course, without chemical significance. Terms in such kinetic triads are, therefore, empirical and may vary with experimental conditions, time, temperature and/or extent of reaction (α). Two decompositions, originally regarded as simple, single, solid-state rate processes, but which were later identified as complex (pairs of overlapping) reactions, are the decomposition of $KMnO_4$ [23–26] (intermediate $K_3(MnO_4)_2$ formation) and the dehydration of $CaC_2O_4 \cdot H_2O$ [44] (concurrent rate processes proceeding at different rates).

Change of reaction stoichiometry within the temperature range of kinetic studies

The decompositions of oxalates of some relatively electropositive cations (e.g., lanthanides) occur in temperature ranges within which the carbonate products become unstable and breakdown. In addition, disproportionation of carbon monoxide can complicate the interpretation of measured rate data [45–50].

Dependence of decomposition rate on a precursor dehydration reaction

The kinetics of anion breakdown in the thermal reactions of nickel squarate dihydrate was shown [51] to depend on the precursor dehydration step. Reproducible reaction rates were obtained only by the use of a standardized experimental technique. The decomposition of cobalt oxalate is sensitive to the temperature at which the salt had previously been dehydrated [52].

Melting with concurrent reactions in solid and liquid phases

If concurrent reactions in solid and melt phases proceed at different rates, when reactant breakdown is accompanied by fusion, kinetic characteristics vary with temperature, α and (possibly with) crystallite size, as has been described for malonic acid [53]. More complicated kinetic behaviour, not obviously represented either as a homogeneous or as a heterogeneous reaction, has been described for the dehydration of *dl*-lithium potassium tartrate monohydrate [54].

Decomposition with melting and/or in a melt

The decomposition of copper(II) malonate proceeds to completion in two distinct rate processes, ascribed to stepwise cation reduction, $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$. The kinetics and mechanisms of both reactions are discussed in [55]. The first autocatalytic process is identified as being promoted by acetate intermediate, present in a viscous melt. The second deceleratory and slower step yields a residual product composed of metallic copper dispersed on a carbon matrix. The kinetic characteristics of other copper(II) salts of organic acids, which also proceed to completion in two cation reduction steps, are discussed in [56].

The decomposition of $(NH_4)_2Cr_2O_7$ was originally identified microscopically as a nucleation and growth process but later work has shown that reaction proceeds in a molten/foam phase, probably CrO_3 [57]. The initial acceleratory reaction is followed by a deceleratory phase, almost certainly involving several concurrent rate processes because intermediates, including NO_2^- and NO_3^-, participate.

Thermal decomposition of *d*-lithium potassium tartrate is believed [58] to proceed at edges of melt droplets by a geometric model, which initially and qualitatively shows some similarities to the active interface of a nucleation and growth process.

Experimental inadequacies

In addition to the above (mainly) chemical reasons for variations in kinetic behaviour, through the influences of secondary controls, limitations of computational technique can introduce further uncertainties into interpretations of rate measurements [6–9]. Factors reducing the reliability of analyses of kinetic data include:

Insufficient experimental data

It has often been incorrectly assumed that all three components of the kinetic triad can be determined from a single non-isothermal set of time–temperature-rate measurements. This is not possible, as shown in [59].

Omission of appropriate kinetic models

Many kinetic analyses restrict data testing to an arbitrarily selected set of rate equations, usually those representing the geometric patterns expected for solid-state decompositions [1]. If an applicable, but unconsidered, reaction model (of the same type) is excluded from consideration, then the standard method of finding the 'best fit', by an error function, cannot successfully identify the course of reaction.

Omission of confirmatory experiments that are capable of corroborating kinetic deductions

Conclusions reached through interpretation of rate measurements by kinetic analyses are made more reliable by confirmatory experiments [6–9], which are not, however, always undertaken. Such tests include microscopic observations of systematic changes of the geometric pattern of interface development during reaction, the recognition of textural changes attributable to melting, etc.

Computational inadequacies

The computational method used, whether by hand or through a computer program, must ensure that the rate constants used to calculate the Arrhenius parameters are defined in the correct units of $(\text{time})^{-1}$. It should also be confirmed that the apparent magnitudes of *SA* and of *SE* obtained do not vary widely with the kinetic model used in their calculation and that such values obtained from a single data set do not exhibit compensation. Computational shortcomings accounting for inconsistencies that appear in calculated kinetic parameters have already been discussed in detail [6–9].

Comment

The above survey, of representative rate studies reported for the thermal reactions that occur on heating initially solid reactants, demonstrates that kinetic behaviour is not a fundamental and unchanging property of each individual reactant. Rate characteristics often vary with both form and history of the sample studied [3, 4], with conditions used during experimental measurements, with reaction rate and with other factors, such as preirradiation. Apparent Arrhenius parameters, *SA* and *SE*, and also the kinetic model, $Sg(\alpha)=kt$, (even when correctly) calculated from rate measurements, are not necessarily inherent and invariable properties of the chemical compound studied but rates are often significantly, even considerably, influenced by a variety of secondary controls, in addition to a (possibly) dominant reaction step. It is difficult to understand, therefore, why so much effort has been invested in measurements of 'kinetic triads' (also kinetic 'duos', activation energy and kinetic model, etc.) when these parameters have no confirmed or identifiable fundamental chemical significance. The continued collection of such data extends no recognisable pattern of chemical reactivity, the conclusions are rarely considered in the context of the wider chemistry of the reactant components, the results provide no insights into the nature of the chemical properties that determine reaction mechanisms, etc. [6–9].

The term 'activation energy' [60] was introduced to identify, and to quantify, an energetic activation step, the energy investment, *E*, required to generate the specific transition state 'molecule' [2]. Through the unstable intermediate envisaged, reactants are transformed into equally fully characterised products. The evidence required to justify the use of this detailed model for reactions at a solid–solid contact interface, or even at a crystal surface, is not available, as already stated. Consequently, the term 'activation energy' is not correctly applied to solid-state decompositions because this application of the TST model lacks the necessary experimental foundation. Removal of this central and familiar feature (*SE*) from the kinetic analysis of crystolysis reactions would open the way to an overdue reassessment of the fundamental theory of the subject. It would also allow the interpretation of experimental data to be based on a more substantial set of theoretical premises than is currently offered by the assumed (but hitherto inadequately confirmed) parallels with homogeneous reactions. Critical reconsideration of the precise significance of rate data, as usually measured, would enable the kinetic theory, and its use in mechanistic interpretations, to be reappraised and applied realistically, including the roles of secondary controls.

Recognizing that various secondary factors are capable of influencing the kinetics of many crystolysis reactions (e.g. of $CaCO_3$ and other solids, as reviewed above), it is not unexpected that these also participate in determining temperature coefficients of reaction rates [32–37]. What is surprising is that so few attempts have been made to correlate these variations with systematic changes of reaction conditions and/or the effects of selected secondary controls. Similarly, the detection of compensation behaviour has often been deemed worthy of report but, again, explanatory reasons have not been sought by extending experimental investigations of kinetic data [11, 61].

Melting

It can be argued that crystal melting is a particular type of solid-state decomposition: on heating, primary valence forces bonding the crystal constituents are redistributed. Unlike a crystolysis reaction, this phase transformation is completed at constant temperature, the melting point, and fusion rates are not amenable to kinetic (and mechanistic) studies. The relationship between crystal melting and decomposition has recently been discussed [62] in reviews of the melting of metallic elements [63] and of alkali halides and their mixtures [64–66]. This behaviour pattern is mentioned here to emphasize that melting, occurring as a result of accumulation of energy within the closely packed assemblage of component particles in a coherent crystal, is a quite different process from the homogeneous chemical changes in gases. Consequently, it is worth considering whether the relationship of melting and solid-state decompositions is closer than has been accepted hitherto, Scheme 1 of [62].

Theories of kinetics and mechanisms of crystolysis reactions[****]

Temperature coefficients of reaction rates

It is proposed here that, if measured rate data were routinely analyzed more comprehensively and sensitively than has been the recent practice, the quantitative results obtained might increase the amount of useful kinetic information available concerning all the significant influences that determine an observed reaction rate. At present, following the methods of homogeneous kinetics, analyses of rate data assume, almost invariably, that data fit the Arrhenius equation, from which *SE* and *SA* magnitudes are calculated. The values thus obtained often appear to be accepted (implicitly) as having achieved the principal goal of the kinetic study. Some investigations go one stage further by regarding such results as providing evidence from which the nature of the rate-limiting step in the overall reaction may be deduced. Confirmation that a measured rate has been determined exclusively by a single dominant (chemical) process [32, 33] is not, however, always provided.

An alternative view, advocated here, is that we should, in principle, measure and interpret kinetic data that has been obtained in sufficient detail to be capable of providing comprehensive insights into all rate characteristics. In this approach, every contributing rate control would be identified and its influence measured individually. Such an ideal situation might be achievable by quantitative measurements of all detectable variations of the temperature coefficient of reaction rate with α, time, temperature and, equally importantly, with appropriate changes of conditions in the reactant environment. This analysis would replace the conventional (Arrhenius model) representation of *SA* and of *SE* values in favour of a more direct, quantitative investigation of the specific roles of all participating secondary controls (mentioned above). Changes of kinetic behaviour found to arise from systematic modifications of experimental conditions could then be used to identify, for quantitative measurement, every factor that has been shown to be active in influencing the rate of the target reaction. Kinetic measurements would include determination of the sensitivity of reaction rates across a range of experimental conditions, including the procedural variables [34]. The results from such extended experimental observations must be more significant chemically, in characterizing reactivity, rate controls and mechanisms, than a single overall empirical value of *SE*.

This more intensive approach to kinetic investigation would replace the conventional assumption that the Arrhenius model is the only method for the interpretation of temperature coefficients of reaction rates and where *SE* always possesses the same theoretical significance as in homogeneous reactions. In contrast, the *SE* value, when determined under conditions shown to exclude contributions from secondary controls, perhaps provides an absolute measure of

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[****] Some recent novel approaches to the kinetic analyses and interpretation of rate data are discussed, including the significant theoretical proposals by Boldyrev and by L'vov.

solid reactivity and might be accepted as the rate of a dominant chemical step, at a surface or interface [32, 33]. The CRTA method of rate measurements [67–69] may provide the most reliable kinetic data by eliminating, or perhaps minimizing, contributions from secondary controls that are relatively more intrusive when other techniques are used.

The isoconversional approach to kinetic analysis has been widely applied in determinations of the variation of *SE* (here referred to, however, as 'activation energy') values with α [70]. This data analysis technique could perhaps be advantageously applied in quantitative investigations of the dependence of variations of temperature coefficient of reaction rate with changes of experimental conditions and thus be used to elucidate the influences of secondary controls on kinetic behaviour. Consequently, instead of accepting *SE* magnitudes as a kinetic conclusion, the variations of *SE* with pressures of gases present, sizes of reactant particles, etc. could be used to characterize each of the various factors that influence the rates of the chemical changes. The decomposition of ammonium perchlorate, studied by this method [71], is, of course, a complicated rate process and further aspects of this set of interrelated and interdependent reactions remain to be resolved [16].

Recently, some evidently sophisticated mathematical models for the kinetic analyses of solid-state type reactions have been proposed [72–74], involving physical principles that differ from those previously applied to reactions of this type. This approach is described as 'semi-empirical' and the applications of the new model appear to be tested by demonstrations of the excellence of fit that the novel equations provide for selected examples of previously published kinetic data taken from the literature. The reports of these comparative analyses devote little attention to consideration of the precise methods whereby the original measurements were obtained, the precision of the data values used in the comparisons, the detailed chemistry of the reactions concerned and reasons why these particular examples were selected. Remembering the diverse factors that may influence kinetic behaviour, as detailed above, this author wonders whether the possible roles of secondary rate controls were examined before developing the new models to provide the improved accuracy claimed to represent these kinetic behaviours. It is essential to demonstrate the reliability of the chemical kinetic data selected, and define how the system is appropriate, before it is used to test a new theoretical model. It is also reasonable to expect confirmation that all possible simple explanations of the observed chemical characteristics have been considered and excluded before proceeding to advocate the development of a novel and possibly more complicated theory. The experimental background provided in these reports [72–74] seems not to address these concerns adequately. The problem in interpreting such data is not the generation of hitherto untried mathematical forms but is to provide a reaction model capable of verification by observational evidence that is complementary to the fit of the data to a conventional rate equation. Taplin [75] has emphasized that, instead of using empirical relationships in this field of kinetic analysis, equations verified by additional independent measurements for the reaction system are to be preferred.

Comment

It is concluded, from the above survey, that useful contributions to solid-state chemistry can realistically be expected from experimental measurements of the systematic deviations of representative *SE* (etc.) values with other variables (and from constancy). If the *SA* and *SE* values obtained for appropriate crystolysis reactions, under conditions selected to reduce or to eliminate the influence of secondary controls, do not show detectable, systematic variations as reaction progresses, then it is possible that its rate is determined by constant controls. From such observations, it may be possible to elucidate chemical steps in the reaction mechanism. Precise measurements of rates, and the magnitudes of their variations with temperature, for selected, well-defined, chemical processes, e.g., interface advance, nucleation, etc., could then contribute to the characterization of the properties and nature of the solid-state chemistry involved. The value of measuring reaction rates under conditions where control is demonstrably identifiable with single, dominant rate process at an advancing interface, has been discussed for calcite decomposition [32, 33]. If, alternatively, values of kinetic parameters show appreciable variations with α, rate, etc. and/or with reaction conditions, then the form of these changes may enable deductions to be made about which secondary controls influence the overall rate of the interface processes. This is possible, however, only if the theoretical implications inherent in the accepted usage of the (homogeneous model) Arrhenius parameters are removed by accepting that chemical controls other than a single, dominant rate-limiting step can exert significant influences on reaction rates. For such processes, *SA* and *SE* values are empirical.

The above critical survey has identified serious problems that arise in the interpretation of rate data but remain unconsidered by many researchers when reporting kinetic and mechanistic studies of crystolysis reactions. Authors in this field are either unaware of, or ignore, the considerable limitations inherent in the conventional theory [6–9] by publishing results that make little or no contribution to the organic growth of a structured scientific discipline. Automated equipment provides kinetic data deceptively easily. What appears to be difficult to accept, in this field, is that rates measured for overall chemical processes do not always represent the occurrence of a simple, easily interpreted reaction. Moreover, such data may be insufficient to, or inherently incapable of, yielding dependable information about the reaction mechanism, the controls of reactivity and/or the fundamental chemical properties of the reactant. Many recent papers do not appear to consider the possibility that (assumed trustworthy) conclusions (such as the kinetic triad), computed from observations recorded by automated equipment, can be no better than the reliability of the experimental observations made and the programs used to analyze them. Consequently, many kinetic results must be accepted as being of empirical value only. Some of the problems reviewed in [6–9] can be summarized:

- Data given by automated equipment are often insufficient to characterize all aspects of the reaction chemistry involved, including concurrent/consecutive rate processes, determining the stoichiometry of complex reactions, distinguishing the roles of nucleation and growth steps, identifying the involvement of melting, etc.
- The importance of secondary controls, significantly influencing overall reaction rates, may not be recognized, i.e., reaction reversibility, reactant self-cooling, etc.
- Kinetic analyses do not include consideration all the possible mechanisms that may be relevant, e.g., melting, reversibility, complex reactions, etc.
- Kinetic terms used are often inadequately, or erroneously, defined: rate constants may be composite quantities [11, 61].
- Application of the theory of reaction kinetics to solid-state decompositions contains assumptions that have not been adequately justified, including the identification of reaction precursors and any essential intermediates, the nature of the activation process, the significance of apparent E values, etc.

Theories of solid-state decompositions and chemistry of reactions in solids

Stagnation in this subject [76] may have arisen through the unwillingness of many of its practitioners to accept that (*i*) solid-state rate processes are not necessarily simple, one-step reactions and (*ii*) the theory of homogeneous reaction kinetics cannot be applied unchanged to crystolysis reactions. The above survey provides ample justification for both of these generalizations. Nevertheless, despite strong literature criticisms, e.g., [6–9], about the validity of current techniques for rate data analysis, papers reporting kinetic conclusions, which ignore the well-established and important deficiencies in the experimental and computational methods used, continue to be submitted for publication. It is, therefore, appropriate to mention, yet again, that more rigorous approaches to the investigation of solid-state reactions offer greater promise of obtaining insights into the chemistry of these interesting reactants than has yet been shown to be achievable by the mathematical analytical methods embraced so enthusiastically by so many thermal analysts. If we can set aside, at least temporarily, the superficialities and empirical irrelevancies of recent years, it is certainly worth exploring the merits of reorienting research efforts into potentially more profitable directions, already strongly advocated by some authors. An essential, perhaps unwelcome, feature of these alternative methods is that greater investment of effort will be required. The present comfortable reliance on ‘machine recording and machine computation’ will undoubtedly have to be superseded by more diverse, imaginative and (probably) labour-intensive experimentation, if progress is to replace the current stagnation [76].

Published theoretical models, that are unfortunately and inexplicably cited only rarely in the recent literature, have already shown their considerable potential abilities to provide tantalizing and novel insights into the elucidation of the mechanisms and controls of crystolysis reactions. These include the two, distinctive and entirely independent, approaches advocated by Boldyrev and by L’vov. (These are mentioned here, and discussed below, in chronological, as well as alphabetical, order.) It is interesting that these distinguished and highly productive researchers have addressed different objectives in developing the methods they propose to explain reactivities and mechanisms of solid-state decompositions. Moreover, their different reaction models remain unreconciled and neither approach had yet attracted the support of a majority of the other authors active in this field, who, in general, ignore both, while continuing to use only the more conventional and familiar, but limited, methods of kinetic analyses. The present author can identify no common ground that is likely to resolve this (three-way) impasse. I can, however, draw attention to the lack of progress, which is attributable to an (apparently congenital) unwillingness by everyone, active in this subject area, to consider the viewpoint of anyone other than himself. Critical, or supportive, comments across the artificial but effective ‘boundaries’ that separate the different ‘camps’ should be a first stage in resolving the disparate and independent views about the controls and mechanisms of crystolysis reactions that are so evident in the literature. Because substantive exchanges of opinions appear to be (?self-)inhibited, the subject has become fragmented, theories remain restricted in application and there is no discernible evidence of any systematic or overall progress in any particular or preferred direction. The relatively few attempts that have been made to resolve the obvious inconsistencies and limitations in theories that are applied to crystolysis reactions have remained generally ineffectual [6–9]. We apparently remain 'in stato stagnensis' [76].

In conformity with the (seemingly established) convention that distinctive ideas evolve separately, short accounts of the theories proposed by Boldyrev and by L'vov are given below. Unfortunately, neither model has been critically tested nor significantly developed beyond the immediate research groups concerned, but also (and equally surprisingly) neither has attracted serious adverse comment. My intention here is to juxtapose these two quite different theoretical approaches to bring to the attention of all researchers, active in this field, essential features inherent in the two quite different reaction models. Potentially very considerable benefits could result from (at least partial) reconciliation of these alternative and contrasting approaches, which are arguably, though perhaps only superficially, complementary. I cannot, of course, express these ideas with the clarity of either Author mentioned and, therefore, I give citations to provide access to representative articles, in which the theories are explained authoritatively and comprehensively by each advocate himself. The following brief summaries mention only essential aspects of these theoretical models, proposed to account for thermochemical properties of solids.

Some theoretical contributions by Boldyrev

As already mentioned, Boldyrev stated positively [3, 4], very early in his long and highly productive career [77], that he was unconvinced that kinetic data provided evidence, which could accepted as sufficiently reliable, or suitable, for use in the formulation of reaction mechanisms. Nevertheless, in his detailed elucidation of the reactivity controls in the decompositions of a range of solids, notably including silver oxalate [15] and ammonium perchlorate [16], kinetic data are used to a limited extent and interpreted with the support of other complementary observations. Subsequently and consistently, Boldyrev has continued to maintain an essentially chemical tradition in his many investigations of the reactivities of solids and in discussing the mechanisms of their thermal breakdown reactions. This approach recalls many characteristics of the research methods that were widely practised before the advent of thermal analysis. His experimental investigations include the use of physical measurements such as electrical conductivity (the roles of specific defects), X-ray crystallography and other diffraction methods [18] (crystal structure, topotactic behaviour and strain), microscopy (texture, interface topology), etc.

The two papers cited [15, 16] report particularly comprehensive and intensive examinations of the thermal chemistries of the target substances and also identify those aspects which still require further observations to elucidate and to confirm details of the mechanisms formulated. Furthermore, the development of nuclei in these two particular reactants, $Ag_2C_2O_4$ and NH_4ClO_4, are both shown to involve crystal distortion, within which imperfections are generated in advance of the notional interface, so that reaction is initiated at nucleation sites located within a region of strained reactant structure. This mechanism is more complicated than that portrayed by the classical model and represents chemical and physical changes as occurring within a zone, which results in the formation of 'nucleus swarms', rather than reaction at an idealized (perhaps planar) contact (continually advancing) interface. Kinetic observations are shown to be consistent with the pattern of behaviour elucidated by detailed investigations of the texture throughout the whole reaction zone and with the specific imperfections identified as participating in the promotion of the chemical change. Most notably, and in stark contrast with most literature reports, the magnitudes of calculated activation energies are regarded as being less important, their significances remaining uncharacterized.

Only two representative reactions are mentioned here, to exemplify this approach, but the extensive publications by Boldyrev and his colleagues [77] include studies of a range of other thermal reactions involving the decompositions of selected relatively simple and well-defined crystalline compounds. Again appropriate chemical and physical methods have been used to elucidate the reactivity controls and mechanisms of these decompositions. The detailed and wide-ranging reviews cited [15, 16] demonstrate that careful, extended and systematic analyses of comprehensive and complementary information are required to elucidate all the processes participating in the chemical changes involved, particularly within the active interface zone. Thus, valuable insights have been obtained into the detailed chemistry of selected solid-state reactions. Mechanism formulations are difficult with details of the behaviour patterns described, including the significance of the *E* values, remaining incomplete.

Some theoretical contributions by L'vov

The physico-chemical approach to interpretation of the kinetics and mechanisms of thermal decompositions of solids identifies the rate of reaction with the rate of reactant volatilization [78]. The primary step in salt breakdown is represented as congruent dissociative evaporation of the reactant with immediate condensation of the low-volatility product, the energy released being distributed, approximately equally, between reactant and product phases. Vapourized molecules, which may differ from the final products detected, reach complete equilibration with the condensed phase on each collision. The evaporation rate can be calculated from the Hertz and Langmuir theories (which replace the Arrhenius theory in this treatment) and enables the specific enthalpy of volatilization (corresponding to the *E* parameter) to be calculated for systems where the necessary thermodynamic data are available.

This identification of an evaporation step as rate determining in solid-state decompositions was developed from L'vov's extensive studies of volatilization processes, investigated during his researches in atomic absorption spectroscopy [79–82]. The physical approach was applied to decompositions of eight metallic azides in 1997 [83]. Kinetic studies have shown the method to be equally applicable to the decompositions or to the sublimations of many and diverse, but relatively simple, substances in vacuum [84]. The review article ([78], p. 120, item 3) states that 'The physical approach has been successfully applied to interpretation of the kinetics of sublimation/dissociative evaporation of more than 110 substances from 20 different classes: …'. It should, however, be stated, in the context of the above emphasis on the unreliability of many reported kinetic results, that L'vov has always discussed the trustworthiness of the rate data used in his comparisons and, in particular, the significance of any self-cooling. Reversibility is accommodated by considering whether reactions have been studied in the absence of volatile products (the equimolar evaporation mode) and such rate processes are distinguished from isobaric reactions, occurring in an excess of a gaseous product [78]. The latter kinetic control has been investigated [85] through quantitative comparisons of dehydration rates, both in vacuum and in the presence of water vapour, for twenty-two hydrated salts.

Comprehensive accounts of this theory have recently been published in Russian [86] and in English [87]. Emphasis throughout L'vov's many publications has always focussed on the central significance of the *E* parameter and the identities of the species formed in the initial volatilization step. The chemistry of any reactions following the initial step can then be elucidated from the final products identified. Less attention has been concerned with the textural, structural, topotactical, etc. properties of solid-state reactions and the model appears not to consider precursor processes. With this emphasis on *E*, it is not readily obvious how the model relates to the more familiar features of solid-state reactions, the patterns of generation and growth of nuclei, or how it may be applied to more complicated rate processes involving concurrent reactions, e.g., [26]. These may be reasons why '…..other workers have ignored the CDV mechanism in studies of the decomposition kinetics' [85] (CDV – congruent dissociative vaporization). Certainly, these proposals have not received the interest (neither supportive nor critical) that might reasonably have been excited by the appearance of a novel reaction model in a field where adequately founded theoretical explanations of observed behaviour are in short supply.

Discussion

This survey reviews a subject area, solid-state thermal decompositions, which continues to attract considerable interest and is often regarded almost as a distinct discipline. Many reports of kinetic and mechanistic investigations of crystolysis reactions continue to appear, adding to the already extensive literature. Critical examinations of the contents of these articles are, however, less than encouraging. New studies tend not to contribute to the systematic growth of an ordered branch of scientific knowledge because so many contributions appear isolated and linked to the remainder of the subject only by the use of a common experimental technique or computational method. The chemical features of the systems selected for investigation are not usually characterized and discussions do not systematically correlate results for particular decompositions with other comparable reactions. There is no widely applicable and generally accepted theory capable of providing a systematic foundation for classification of results obtained or suitable for predicting behaviour of hitherto untested systems. Currently, it is difficult to detect either the advance of scientific ideas or any trend of coherent development in this subject.

Unifying theories, essential to consolidate and to unify the study of crystolysis reactions as a coherent, evolving science, are currently not widely accepted as being applicable throughout the subject. The reliance on incompletely substantiated concepts 'borrowed' from homogeneous kinetics has become partially concealed beneath the fashionable and dominant interest in thermal analytical methods but, nevertheless, remains in vestigial form behind the (unstated) realization that they are probably not applicable. This approach continues in use mainly because the older theories of kinetic analyses are easily applied and because computers can generate a statistical veneer apparently concealing shortcomings in the calculated parameters and thus lend an apparent authority to the conclusions. However, as described above, without additional observations and/or specialized programs, computers cannot overcome the forgotten fact that many measured reaction rates are subject to multiple controls. Consequently, the reported kinetic conclusions from such minimalistic investigations (e.g., the kinetic triad) are often empirical and applicable only under the specific conditions of the particular experiments described.

There are several ways of resolving this impasse, all of which require greater input into the design of experimental programs and/or the expenditure of a larger effort in the collection of all relevant experimental data. The 'simple' approach has simply not worked. Ways forward, meriting further consideration, include the following.

- Kinetic investigations may necessitate determinations of the rates of reaction proceeding under an appropriate range of experimental conditions followed by detailed analyses of these observations to identify each of the rate controls that participate. Such analyses include distinguishing the roles of nucleation and of growth, measuring the effects of reversibility, estimating self-cooling, detecting unusual mechanisms, undertaking appropriate confirmatory tests, etc.
- Detailed physical and chemical characterizations of the reactant are required to identify textures, crystal structures, imperfections, strains, participating components, etc. before and after partial reaction, with particular reference to properties and structures of the active reaction zone. Complementary measurements may be required to determine conductivity, as well as textures, through microscopic and diffraction observations: their design should be based on imaginative interpretation of all the evidence that can be obtained. It is particularly important to investigate those features of behaviour that specifically relate to the mechanism being considered: e.g., Boldyrev [15, 16].
- Kinetic studies, to measure E, may enable the processes controlling the decomposition rate to be deduced: see L'vov [78, 86, 87].

Extended experimental foundations offer opportunities to obtain additional, alternative and augmented insights into crystolysis characteristics. Perhaps this wider approach can remove some of the uncertainties that have arisen during the recent period of excessive preoccupation with the exploitation of mathematical methods that have been designed to use 'fewer' observations to obtain 'more' conclusions [6–9]. This policy has been followed for many years and the subject appears to have reached a situation in which progress has become slow (or absent). Perhaps now we should agree to reconsider, and expand, the experimental input to the subject. The fashions of the recent past need to be replaced by more rigorous and intensive laboratory techniques, if we are to increase our understanding of the solid-state science applicable to these often relatively complicated, but chemically distinctive, reactions.

Personal remarks

After more than half a century working in this field, I am now retiring. This is intended to be my final publication concerned with crystolysis reactions. When I started research in 1955, there was great optimism about the future of this subject, following publication of the 'Garner *et al.*' outstanding, 'break-through' work [88]. Unfortunately, the momentum of this initiative was not maintained and many of the high hopes felt at that time still remain unrealized. The approaches to the subject, then seen as offering promise, have since been replaced by the alternative, and ultimately not entirely successful, techniques of thermal analysis. At about the same time, the uncomfortable recognition that the theory of reaction kinetics then being used was (and still is) of limited value in consideration of crystolysis reactions has stultified development of the subject. Perhaps a reversion to these earlier and more chemical and physical investigative methods, complemented by the advanced experimental techniques developed by the thermal analysts and computer scientists (but omitting current theory), can now open a way forward. Perhaps, more diverse and accurate observations may identify novel and promising approaches to theory development that would model, more realistically, the reactions of solids. Perhaps also the proposals by Boldyrev and by L'vov can strengthen the theoretical foundations of the subject, leading to a greater understanding of the chemistry of crystolysis reactions. Perhaps it is time to become optimistic again…

Afterword

My answer to the rhetorical question used as the title of this article ('What can we learn about the mechanisms of thermal decompositions of solids from rate measurements?') is that we usually learn less than we think (or hope) we have. But there is always the realistic possibility that we can (could and should) do better.

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