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AN APPRECIATION OF THE CHEMICAL APPROACH OF V. V. BOLDYREV TO THE STUDY OF THE DECOMPOSITION OF SOLIDS

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Professor Vladimir V. Boldyrev has made numerous important contributions to a wide range of chemical topics, not only limited to studies of the decompositions of solids. Of particular value has been his emphasis on exploring, in detail, the chemical steps participating in the thermal reactions of solids by carefully designed experiments that rely on more observational evidence than the run-of-the-mill collection of overall kinetic data. Some of these major contributions to both the theory and the uses of solid-state reactions are identified here and discussed in relation to his illuminating and fundamental mechanistic studies of the thermal decompositions of silver oxalate, ammonium perchlorate, potassium permanganate and the dehydration of copper sulfate pentahydrate.

Keywords: *ammonium perchlorate, copper sulfate pentahydrate, decomposition of solids, dehydration, potassium permanganate, silver oxalate, solid-state reactions*

Introduction

The total contribution by Professor Vladimir V. Boldyrev towards advancing the understanding of chemical reactions is exceptionally large both in value and in range. Under Boldyrev's direction, the Institute of Solid State Chemistry at Novosibirsk was established and has thrived. This address appears on many important and highly cited scientific publications. A large number of researchers, who were trained and/or gained experience in this Institute, have gone on to develop important research topics and interesting themes that were initiated in Novosibirsk. Subsequently, the subjects and ideas originating in this Centre of Excellence have influenced research work and ideas well beyond the site where Boldyrev's original enthusiasm initiated a Research Institute that established and has maintained a world-class reputation. Selected aspects of these overall contributions, particularly directed towards extending knowledge of solid-state chemistry, are discussed in this short review.

Currently some 800 papers, citing the name Boldyrev as author and/or editor, are listed by Chemical Abstracts, CAS Online, which also includes the names of his many research collaborators. Boldyrev's outstanding research career has been unusually prolonged and still continues, well into its sixth decade, a period during which he has remained consistently productive. This is strikingly illustrated by the distribution of dates on his publications, as shown by the histogram in Fig. 1, evidence of a truly amazing overall achievement. Boldyrev's total scientific output is so extensive and diverse that it cannot be realistically or comprehensively appraised in a short article. We have, therefore, selectively focused only on those studies which are concerned with chemical aspects of the thermal decompositions of solids. Many of the original publications are in the Russian language

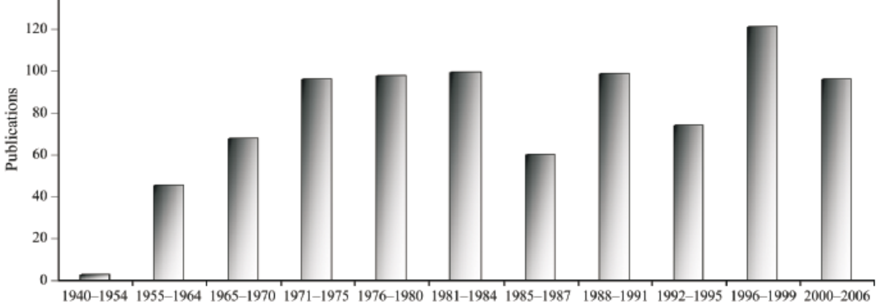

Fig. 1 Time distribution of dates on the papers published by Boldyrev

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

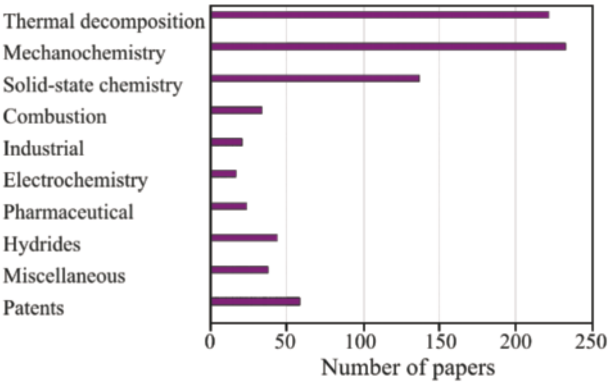

Fig. 2 Distribution of subjects in publications authored, coauthored and/or edited by Prof. Boldyrev (the classification of topics is slightly arbitrary)

and, where an English version has not appeared, we have used a translated Abstract for this review.

A classification of the subject matter contained in these approximately 800 publications is shown in Fig. 2. The research topics have been grouped, somewhat arbitrarily, into the categories: thermal decomposition, mechanochemistry, solid-state chemistry, combustion chemistry, industrial chemistry, electrochemistry, pharmaceutical chemistry, hydrides, miscellaneous studies (i.e., diverse 'other' topics) and patents. There is a considerable overlap between these categories and we note the particularly large contribution to mechanochemistry and the extensive list of patents. However, the dominant feature of Boldyrev's work is identified here as his contribution to solid-state chemistry, particularly including the thermal decompositions of crystalline reactants, which we have selected as the subject for our survey (and is our principal research interest).

Thermal stability is one important facet of the broader topic of reactivity of solids, which includes the properties and processes that are involved when solids react with other solids or with liquids or gases, and when solids promote the reactions between gases adsorbed on their surfaces, etc. In spite of numerous conferences on the topic of reactivity of solids [1], progress in elucidating the chemistry of these types of reactions has not been spectacular. Similarly, research more specifically concerned with aspects of thermal stability of particular solids, illustrated by many of the contributions to thermal analysis conferences [2], has not produced the progress that was confidently anticipated some decades ago.

Boldyrev, appraising the intractable nature of the subject, [3] has commented that 'Studying reactivity of solids resembles in some respect a long trek across a desert in search of a source of water. Sometimes it seems to us that at the horizon there is an oasis with water, trees and flowers. Many people rush in the direction of the oasis, leaving a wide road behind them. Those that follow the running crowd look at the road and think that the fact that the road is well-trampled is the best proof that it leads to a real oasis. And only those who were the first to start moving in the direction realize that the oasis is only an optical illusion'. Although this comment was published in 1993, other researchers have subsequently reached similar conclusions. This rather pessimistic view modestly hides the fact that Boldyrev himself has been a major contributor in the search for 'the oasis'. Although he feels that he may, on occasion, have led some researchers in directions that were subsequently found to be fruitless, many of us have been inspired by his work in attempting to solve the important challenges that he has identified. The objective remains important even where there has been disagreement on the best direction ('the road') to be taken for the (re)search.

Even with our self-imposed restriction, in reviewing here only thermal decompositions of solids, we have found it necessary to limit our coverage to representative substances from the extensive range of publications in which Boldyrev has reported investigations of the thermal reactions of numerous different crystalline reactants. This topic has been a central, life-long interest throughout his research career: it featured in the earliest studies that established his international reputation, it was developed continuously during subsequent years and it has been the subject of his most recent reviews.

The objects of this survey are to identify some of the significant and valuable research reported by Professor Boldyrev to draw attention to his most important theoretical ideas, and to consider the role of his work in advancing our understanding of the chemical changes that occur on heating crystalline solids. We start by selecting a particular review paper [4] for detailed consideration, because this provides a unifying theme that links and exemplifies Boldyrev's contributions to the theory of this subject and can be related to his equally valuable studies of the solid state decompositions of other reactants. We believe that the critical survey: 'The thermal decomposition of silver oxalate' [4] is one of the most exhaustive and detailed mechanistic analyses of the chemistry of any solid state decomposition reaction that has appeared in the literature. While this choice is somewhat arbitrary, reflecting our own interests in this subject, the account of the publications relating to thermal breakdown of $Ag_2C_2O_4$ is comprehensive, clearly written and uses measured data derived from an exceptionally varied range of experimental observations. The detailed reaction model developed, including identifications of work 'still required', represents a masterly and coherent synthesis of all the information available. This article is a model survey for anyone interested in attempting to determine the factors that control the reactivities of solids and to identify the physical and chemical steps by which a solid reactant is converted into products. The information contained in this analysis, its logical presentation and the critical interpretation of the diverse data considered add significantly to our understanding of the chemistry of all crystalline reactants. Moreover, the methodology underlying this research is of great and general value because it emphasises the use of complementary experimental approaches in obtaining the comprehensive and complementary observational evidence that is required to formulate mechanisms of thermal reactions occurring in solids. In spite of the development of many modern and sophisticated analytical techniques, studies of crystolysis reactions [5] in recent years have tended to focus too heavily on the interpretation of kinetic data (within a very restricted set of kinetic models), using few supporting observations to confirm the conclusions reached.

The 'chemical' approach, generally characteristic of Boldyrev's work, focuses interest on bond rupture/formation steps, the possible participation of intermediates, the characterization of both reactant and product(s), the influence of additives on the nature and rates of reactions that take place, etc. The silver oxalate review [4] is one of the most complete and successful applications of the use of multiple complementary laboratory investigations available. Furthermore, Boldyrev has confirmed the wide applicability of this approach, by making significant contributions towards understanding the stability controls and mechanisms of breakdown of diverse crystalline reactants: including ammonium perchlorate, potassium permanganate, copper sulfate pentahydrate and many other solids.

As is amply demonstrated in Boldyrev's papers, reporting mechanistic studies of the thermal behaviour of the individual reactants he has selected for study, the interpretation of experimental observations for solid state decompositions is not a straightforward exercise. Where several steps participate in and contribute to overall change, the contributing reactions may be many, interlinked and complicated. The active reaction zone, the reactant/product interface within which some chemical changes preferentially occur [5], is often inaccessible to direct investigation. Measurements obtained by different experimental methods, or by using different properties to determine the progress of a reaction, may lead to different apparent conclusions, and such evidently alternative behaviours may be difficult to reconcile. Few consistent trends of chemical characteristics, linking the properties of different reactants, have, so far, been found. Given this degree of uncertainty, it is not unexpected that different researchers have reached contrasting conclusions about the reactivity controls, chemistry and/or mechanisms of thermal decomposition, for some of those reactants which have been the subject of multiple studies. In particular, if a liquid is involved, perhaps as an essential intermediate and perhaps in small quantities, in what initially appears to be a solid state decomposition, this may be difficult to detect and to demonstrate conclusively.

From his studies of many individual reactions, Boldyrev has identified several important fundamental models and principles, that are capable of wider application to all (or, to most) solid-state thermal decompositions. The ultimate objective of this work has been to identify the controls of reactivity and those mechanistic steps (on the molecular scale) which contribute in the transformation of reactant into product. The concepts, mentioned below, are valuable in extending the general theory of the subject (an aspect of solid-state chemistry that is in need of development [5]) and are briefly reviewed here:

- The reaction interface, topochemistry, localization and autolocalization: the tendency for many solid-state reactions to proceed preferentially at an interface,
- Topotaxy, reactions in which the product crystal axes are oriented with respect to those of the reactant from which it was formed,
- Crystal defects, structural imperfections, and their role in decompositions,
- Irradiation, the effects on reactions of crystals, and
- Mechanochemistry, decomposition resulting from mechanical treatment of the reactant and the role of physical activation on subsequent thermal reactions.

Contributions to the theory of solid state decompositions

The reaction interface

Boldyrev has discussed the properties of the reaction interface [4] in detail to establish the reasons why chemical changes occurring in crystals often proceed preferentially within a zone of locally heightened activity. He has considered the roles of: (*i*) the structure and properties of the reactant/product contact, including imperfections, product crystallization and topotaxy, (*ii*) the species participating in the reaction(s) and their mobilities, including both constituents and structures of the reactant and the product phases, interstitial species and the other defects, (*iii*) bond rupture, redistribution and/or formation steps, (*iv*) the significance of self-heating (cooling) on reaction rates and (*v*) how the interface is initially generated, the nucleation step.

The thermal decompositions of inorganic solids were classified by Boldyrev [6–8] into two main groups: those reactions that proceed without electron transfer and those which proceed with electron transfer (redox reactions). Each group is divided into subgroups according to the mechanism of charge transfer and the decay modes of the unstable species or of the radicals formed during the reactions (Fig. 3). The roles of the different types of macro- and microscopic defects in the solid are related to the type of reaction that occurs.

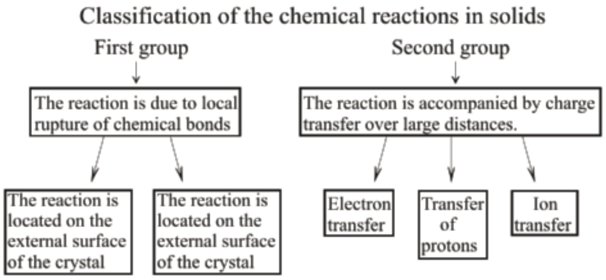

Fig. 3 Classification of thermal decompositions of solids [8]. (With permission from Elsevier.)

Topochemistry of reactions of solids [9–13]

Reactions in solids involve atoms, ions or molecules retained within a coherent and rigid structure and these constraints influence the course of the chemical changes that occur on heating. Consequently, and unlike homogeneous reactions, reactivities of solids often depend on their prehistory. Because of the defects and/or damage that are invariably present, crystals can ‘have a good memory’ [9, 10], resulting from the individual conditions of their preparation, storage and treatment. For many solid-state reactions, chemical changes take place preferentially within a reactant-product interface that systematically advances into the remaining undecomposed material. The progressive changes of product yield with time are determined by the three-dimensional variations of interface geometry that result from the linear advance of the interfacial zone of active chemical change, where reactant is transformed into product. The rate equation describing the course of reactions of this type cannot [14, 15] readily provide insights into the chemistry of the fundamental controlling step(s). This is an important (but not always recognized) difference from the homogeneous reactions that take place in gas or liquid phase. The geometric [5] kinetic model, deduced by interpretative analysis of measured rate data, can sometimes be confirmed, or identified directly, by microscopic characterization of the spatial form of the intracrystalline interface in reactant samples that have undergone partial decomposition.

Aspects of interface chemistry have also been investigated, more directly, by the use of synchrotron radiation [16–18]. To study the reactant/product interface in situ, it is necessary to have a technique that has adequate resolution both in space and in time. The synchrotron radiation facilities, for X-ray diffraction studies, available to Boldyrev and co-workers in 1987 [16], (Fig. 4), had a spatial resolution of 5x5 μm, a time resolution of 10^{-3} s, a phase sensitivity of 0.01% and a penetration depth of 0.01 to 10 mm. One of their earliest studies was on the formation of nickel hydride. Displacement of X-ray reflections from their equilibrium positions was observed as hydrogen penetrated the nickel metal lattice, forming a solid solution. A dislocation structure was generated and there was strong interaction of hydrogen with dislocations and point defects. Formation of a metastable nickel hydride phase was observed in the X-ray pattern. As the hydride phase grew, the lattice parameter of the nickel hydride increased. During the initial stage of hydrogenation, the nickel metal lattice showed the greatest distortion. When the concentration of nickel hydride reached a maximum, the nickel metal lattice relaxed, accompanied by decreases in defect concentrations and increases in domain sizes. Reflections from nickel hydride were detected when their intensity was only 0.01% of the intensity of the nickel metal reflections.

Synchrotron studies have been particularly valuable in studying the dehydration of hydrates, for example, $CuSO_4 \cdot 5H_2O$ and $Li_2SO_4 \cdot H_2O$ [16], where the thickness of the reaction interface was shown to be approximately 0.1–0.2 mm. The nature of the reaction zone depended strongly on temperature and the H_2O pressure, with its composition and structure varying continuously along the direction of its propagation. Laue photographs of single crystals of $CaSO_4 \cdot 2H_2O$ [17] showed that the thickness of the reaction interface

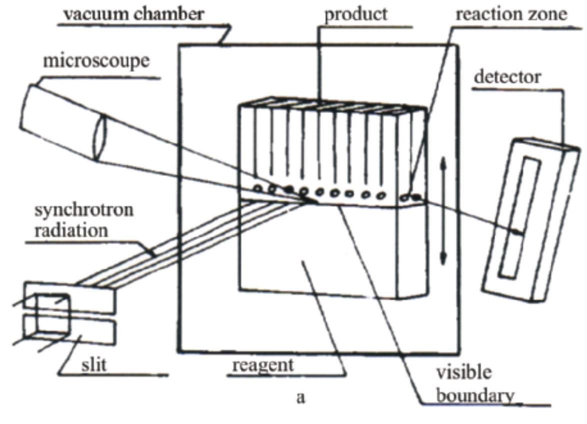

Fig. 4 The experimental arrangement for synchrotron studies [16]. (With permission from Elsevier.)

was similar. The indications were that lamination of the structure took place.

In a study of a phase change in $Ni(en)_2(NCS)_2$ (*en*=ethylenediamine) [18], the transition was found to begin at the centre of the crystal, which was the most imperfect region. Two mechanisms for the phase transition were distinguished: slow growth of monocrystalline nuclei with a non-coherent interface, or rapid advance of a semi-coherent interface accompanied by extensive cracking. Lattice strain generated during nucleation of the new phase was apparent from the asterism of the diffraction spots. Crystal irradiation with an electron dose >80 Mrad led to lattice damage.

Boldyrev's chemical approach to the elucidation of the unitary processes participating in solid-state reactions goes much further than the superficial kinetic analyses that appear in so many recent publications. This more fundamental approach has been used to distinguish and to classify different types of solid-state reactions, thereby providing a useful framework for others to follow. A renaissance in the use of the widest possible experimental base for the mechanistic studies of reactions in solids is overdue. (The proverb quoted in [11–13] appropriately and perceptibly makes the same point: 'All the new is the old well forgotten'.)

Localization [9–13]

Early investigations of solid-state decompositions tended to assume that reaction occurred preferentially at atypical sites, usually identified as crystal imperfections. In the 1960s, Boldyrev discussed mechanisms of solid state reaction and showed that two types of processes could be distinguished [6, 7, 19–21]. Reactions of the first group occurred within one lattice unit, are associated with surfaces and are exemplified by anion breakdown during decompositions of the oxalates, carbonates, etc. of the alkali and alkaline earth metals. Reactions of the second group involved mass or electron transfer steps across distances larger than the lattice unit and are influenced by the crystal bulk and structural imperfections. Such processes include the decompositions of the heavy metal azides and oxalates.

Autolocalization [9, 10]

Autolocalization [9, 10] is the tendency for reaction to occur preferentially in the vicinity of sites or zones where chemical change has already taken place, so that reactivity is increased in localities where some product has already been formed. The effect may not be simple and may involve changes in defect concentrations and/or equilibria, strain and structural modification (where a residual product is formed). The following factors, acting individually or in combination, contribute to autolocalization and are discussed in [9–13]: (*i*) crystal anisotropy, (*ii*) crystal deformation, (*iii*) changes in electron-hole equilibrium at the reaction interface and (*iv*) interaction of a reactant with a gaseous product.

Topotaxy [11–13]

Topotactic reactions yield a solid product in which the crystal axes are specifically orientated with respect to the crystal axes of the reactant. Considerations of the (minimum) structural changes that are required to transform one lattice into the other during the interfacial chemical changes and phase transition enable deductions to be made about movements of the participating species during the interface reaction.

Defects

Another of Boldyrev's major themes has been the importance of crystal defects (Fig. 5) in solid-state reactions, particularly where reactivity can be modified by suitable reactant pre-treatment. This theme is well-illustrated in his monograph with Bulens and Delmon on 'The Control of the Reactivity of Solids' [8]. A later compilation, edited by Boldyrev, 'Reactivity of Solids: Past, Present and Future' also contains much relevant material in chapters by Gutmann and Resch [22] and by Galwey [23]. Boldyrev stresses that little useful knowledge is obtained unless the effects of different kinds of pre-treatment of the reactant, including the deliberate addition of impurities, are examined. Chemical and physical factors become intertwined. Methods for determining the role of crystal defects in reaction mechanisms are illustrated in [9–13] with reference to the decompositions

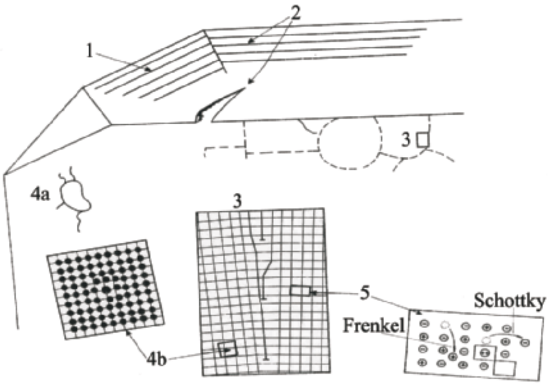

Fig. 5 Defects in solids [8]. (With permission from Elsevier.)
1 – Change of crystal habit, 2 – microcracks and figure of growth, 3 – boundaries and dislocations,
4 – impurities in crystals: a – heterogeneous,
b – homogeneous; 5 – point defects

of silver oxalate, ammonium perchlorate, crystalline hydrates and potassium permanganate.

Skilled use has been made of the etching of partially decomposed crystals to reveal the presence of dislocations and their role in thermal decomposition. Etch figures from the rhombohedral and side planes of NH_4ClO_4 crystals [8] allowed observation of a network of dislocations. The dislocations were present as groups in the vicinity of the growth and mechanical defects. Crystals that had been heated to decomposition temperature before etching showed the clustering of dislocations near the nuclei. This anisotropy of dislocation distributions seemed to be related to the anisotropy of the advance of decomposition in NH_4ClO_4.

The various influences of different selected additives [4] have also been successfully exploited. For example, substitution of the divalent Cd^{2+} ions as an impurity in the $Ag_2C_2O_4$ structure causes a marked decrease in the rate of thermal decomposition of the salt, especially during the initial stages. The addition of <1.5 mol% of Cd^{2+} decreases the ionic conductance of $Ag_2C_2O_4$ whereas higher levels increase it. The addition of Cd^{2+} had no effect on the UV-visible spectra. The decrease in the rate of thermal decomposition of the doped reactant was attributed to the change in the number of interstitial Ag^+ cations caused by Cd^{2+} additions of <1.5 mol%. However, at greater concentrations, it was attributed to an increase in the numbers of cation vacancies, which bind the positive holes, $C_2O^0_4$.

Heterogeneous inorganic additives [3] can affect the rate of thermal decompositions for a variety of reasons. Boldyrev [3] quotes a study, by Saveliev and Zakharov [24], in which oxide and sulfide powders were introduced as mechanical impurities in precipitated silver oxalate. Results showed that contact of silver oxalate with additives having a higher electronic work function (NiO, Cu_2O) accelerated decomposition, while additives with lower work functions (ZnO, Ag_2S) decreased the rate. Metal powders either have no effect (Mg, Al) or decrease the rate (Pb, Fe, Cu).

Organic additives that were electron donors accelerated the decomposition of silver oxalate, while electron acceptors had the opposite effect. Boldyrev and others [4] showed that organic dyes have to be adsorbed from solution to have a significant interaction with the oxalate ion, shown by a decrease in the ionic conductivity of silver oxalate, and an effect on the decomposition rate.

Belous *et al.* [25] measured the luminescence that occurred on exposure of a crystal of silver oxalate to UV light at 77–300 μm. The intensity of the luminescence was proportional to the concentration of the Ag^+ ion and this changed during photolysis and during thermal decomposition.

The effect of preliminary mechanical treatment of silver oxalate [4] on subsequent thermal decomposition was found to be greater than could be explained simply by the surface area increase of the ground reactant. Both the type of mechanical treatment and the atmosphere present (air or vacuum) during treatment, influenced the thermal decomposition. Activation in air led to the formation of some silver oxide and a mixture of carbon monoxide and carbon dioxide.

A thermoelectret state (the appearance of internal polarization during cooling in a strong electrical field) was set up by Mikhailov and coworkers [26] in $Ag_2C_2O_4$ and in Ag_2SO_3. The addition of ions with a different valence, Cu^{2+}, Cd^{2+}, or of a number of organic substances which decrease the ionic conductivity and which increase the thermal stability of the crystals, also decreases the depolarization current. The electret state in these salts is associated with the presence of Frenkel defects, which play an important role in ionic conductance and in determining thermal stability.

Irradiation

Whenever possible, it has proved useful to compare the response of a solid reactant to irradiation with the mechanism of thermal decomposition. Silver oxalate [4] is much more sensitive to UV light than to visible light. Radiolysis generates the same products as photolysis, namely silver metal and CO_2, but, unlike photolysis, is not limited to the surface. Silver metal nuclei are located mainly along dislocation lines. Measurements of the conductivity (another well-used technique) of silver oxalate during X-radiolysis [27] showed behaviour similar to that observed during thermal decomposition. Initial decreases in conductivity result from the depletion of mobile silver ions by the growing silver metal nuclei. Both photolysis and radiolysis are affected by doping but to a lesser extent than thermal decomposition. Various types of pre-irradiation of silver oxalate [4] all accelerated subsequent thermal decomposition. As dicussed further under potassium permanganate (below), there are two main interpretations of the pre-irradiation effects. Prout has proposed [28] that energy accumulated during irradiation is released during thermal decomposition and displaces silver ions from their normal lattice position. Boldyrev's alternative view [29] is that irradiation causes metallic silver to accumulate and that this material catalyzes thermal decomposition. When silver oxalate is thermally decomposed in an electric field [4], constant or periodic, the rate increases. By changing the field direction, the rate of thermal decomposition can be controlled. Mikhailov *et al.* [30] showed that these effects are connected with the ionic stage of the reaction through changes in the concentration of interstitial silver ions.

In a wider study, Boldyrev [31] compared the radiolytic stability at room temperature of crystalline Group I azides, bromates, and nitrates with their respective thermal stabilities. The observed variation of radiation yields (of N_2 and Me^0 in azides, of Br^- and O_2 in bromates, and of NO_2^- in nitrates) was ascribed to a correspondence between the size of radiolytic fragments and the 'free volume' in the crystal lattice. The action of additives on the radiolysis was also examined. The effects of Tl^+, Sr^{2+}, Pb^{2+}, Ce^{3+}, La^{3+}, Pr^{3+} and Nd^{3+} ions on the radiolysis of KNO_3 were attributed to ionic defects produced by these additives in the lattice. These defects may increase the radiation yield due to localization of excitation or to local increases of the free volume in the lattice but they can also improve the annealing of radiation defects. Doping of KNO_3 with additives which can act as electron donors (Tl^+, Ce^{3+}, Pr^{3+}) increased the radiation yields. Doping of nitrates with anions (e.g. SO_4^{2-}) did not change the radiation yields.

Mechanochemistry [32–36]

Boldyrev has made many important contributions to this topic [32–36], that is concerned with the effects of mechanical treatment on the chemistry and reactivity of solids. Several distinct approaches have been used. The reactant crystal may be subject to constant strain (as in a vice or anvil) or intermittent strain (as during crushing in a mill). The decomposition reaction may be studied during the treatment, or subsequently, for a solid reactant that has previously been subjected to a regime of mechanical working.

This extensive subject is of considerable interest in crystal chemistry [32–36] because cold-working of a solid can result in morphological, structural and compositional changes, which result in the introduction of an excess of imperfections. The additional energy, retained by the solid, can be measured by thermal methods. Solids that have been cold-worked may remain thermodynamically metastable and subsequent decomposition can yield products that are different from those observed from the reactions of crystals prepared without energy-introducing procedures.

Thermal decomposition of silver oxalate [4]

113 references are cited in this review [4], about 80% of which are evenly spaced during the period 1955–1984, with a slight maximum interest at about 1967. The older references are used to provide background and to place the work in the theoretical context in which it originally appeared. Boldyrev has contributed much to the elucidation of this reaction mechanism as an author of about a quarter of these papers, most dated between the early '60s to mid '70s. Although the greater proportion of this research appeared two or more decades ago, the very few post-1985 papers add relatively less to understanding of the chemical reactions described.

Although silver oxalate has not been shown to have technological or commercial importance, the photochemistry of this silver salt has been explored, and the decompositions of metal oxalates have been used to prepare heterogeneous catalysts and high-temperature superconductors. Nevertheless, the chemistry of the thermal decomposition of this crystalline compound has been characterized in great detail, through the imaginative use of an unusually wide variety of experimental techniques and principles, in addition to kinetic studies. By publishing this fascinating critical literature survey [4], Boldyrev has reminded the scientific community of the wealth of chemical information that can be obtained through the use of techniques complementary to the measurements of reaction rates. The sections below follow those of the review.

Introduction

Decomposition of silver oxalate is identified as a 'model' reaction, a chemical change believed to involve a small number of relatively simple steps occurring in and between the components of the crystalline reactant and the product, both of known lattice structures. This relatively simple reaction (salt→metal+gas) is placed in the context of three stoichiometrically distinguished patterns of oxalate breakdown, as proposed [37] very early in Boldyrev's scientific career: in his 'Candidate of Science Thesis', Tomsk, 1951. In a later work [38] it was assumed that the initial step in the breakdown of all oxalates is rupture of the C–C bond in the anion. This is the weakest bond and, following distortion of the flat anion, gives two (CO_2^-) radicals that can yield carbonyl carbonate, or revert to the oxalate. If a cation with a high ionization potential is present, the bond rupture is accompanied by electron transfer to yield $2CO_2$, stated [4] to be probable for silver oxalate. This model underlies discussions, throughout this survey, of results obtained from the diverse range of experimental methods used to obtain data from which the reaction mechanism is formulated. The emphasis on the reaction stoichiometry and the identities of the bond rupture step(s) that determine the stability of a crystalline reactant is a recurring feature of Boldyrev's work, traced here to his earliest publications.

Physiochemical properties of silver oxalate

The reported spectral and electrical properties of the reactant crystal are surveyed in detail. The important result, used in the subsequent mechanistic considerations, is the identification of the presence of Frenkel defects, so that the major charge carriers in the $Ag_2C_2O_4$ crystal are interstitial Ag^+ ions.

Crystal structure of silver oxalate

Determination of the reactant structure is potentially of fundamental importance in considering and interpreting the course of chemical changes that are likely to occur on heating. It is shown [4] (after discussing reasons for rejecting an earlier proposed structure for this salt) that the structure of $Ag_2C_2O_4$ contains silver ions closely spaced in pairs (dimers) orientated as 'ribbons' in [100] channels. This is considered significant because the addition of a third atom to a pair may occur as topotaxial growth. The lattice contains channels along which Ag^+ can 'move freely'. Another property of the structure, important in the proposed reaction mechanism, is the proximity of the oxalate oxygen to interstitial Ag^+, possibly facilitating electron transfer (and product CO_2 formation).

Features of the thermal decomposition: the morphology of the initial stage

It is pointed out [4] that kinetic data obtained from volumetric and gravimetric measurements of reaction rates were insufficient to characterize the mechanism of silver oxalate decomposition, which proceeds through an interlinked sequence of electronic and ionic steps. Additional observations from spectral and electrical measurements were required to identify the processes contributing to the overall reaction. The isothermal kinetic behaviour observed for the decomposition varied for different salt preparations. The more highly defective crystals of $Ag_2C_2O_4$ reactant decomposed according to the exponential law, whereas the rates of product formation from crystals with fewer defects fitted the power law [5].

The acceleratory character of the initial reaction was attributable to a nucleation-and-growth process, although the nuclei remained too small to be identified by optical microscopy and could only be observed by electron microscopy. Nucleus growth ceases when particles reach a size of about 0.4 μm, but nucleation continues in their vicinity to form 'swarms'. Detailed examinations demonstrated that nuclei formed along the c-axis of the crystal and were of two types: (*i*) normal silver metal and (*ii*) metal having an expanded lattice, intermediate in spacing between atoms in the metal and the oxalate and oriented with respect to the reactant crystal. Evidence has also been obtained that the electrical conductivity decreases during the early stages of decomposition, which may be due to the incorporation of the charge-carrying interstitial Ag^+ ions into growing nuclei. The continuation of reaction may involve the topotactic transfer of a cation (from the reactant salt) to the metal (product).

These results, together with observations of the effects of reaction environment, preparation method, a wide range of additives (heterogeneous and homophasic) and various types of radiation have all been considered in the formulation of a detailed mechanism for $Ag_2C_2O_4$ breakdown. It is shown that models based on exciton formation [5], oxalate ion breakdown, interstitial ion steps, etc., do not quantitatively account for the measured rate of decomposition. Growth of nuclei to a particular size is, however, consistent with the availability and distribution of interstitial silver ions: the transition of $Ag_2C_2O_4$ into silver metal is a topotactic process. Nevertheless, certain aspects of the reaction are regarded as requiring further investigation, including the role of the C–C rupture step, the 'swarm-like' character of nuclei and their sizes. Consideration of the roles of localization and autolocalization [9, 10], of topotaxy [11–13] and the role of defects, as in this analysis of experimental results, have been continuing themes throughout Boldyrev's mechanistic investigations. Another characteristic feature is the clear statement of the problems remaining unresolved. For this salt no 'rate limiting step' is identified and, therefore, no particular bond-rupture step is associated with an activation energy, a parameter that receives much less attention here [4] than in most other recent papers on this subject in the literature.

Comment

There is evidence that the apparent activation energies for decompositions of different metallic oxalates vary considerably with changes of metal cation present, between about 120–200 kJ mol^{-1} [39]. Values increase systematically with the enthalpy of formation of the metal oxide. Because these variations of the temperature coefficient of reaction rate with composition are significant, Galwey [39, 40] has suggested that the important step in anion breakdown could be rupture of the carboxyl oxygen-cation link, which is a factor in determining salt stability.

Thermal decomposition of ammonium perchlorate [41]

Introduction

During the ’60s and ’70s, the thermal decomposition of ammonium perchlorate (AP) became one of the most intensively and extensively studied solid decomposition reactions. Two of the reasons for this interest were the financial support for work through missile development programs funded by governments (NH_4ClO_4 is a rocket fuel) and fascination with the unique chemical characteristics of this reactant. Boldyrev has reviewed recently [41] the massive and complicated literature concerned with the several distinct aspects of the thermal behaviour of ammonium perchlorate.

The thermal decomposition of AP is a nucleation-and-growth process [5], which has been studied in two temperature ranges, below (450–513 K, the ‘low temperature’ reaction) and above the crystallographic transition at 513 K. Decomposition is invariably accompanied by salt sublimation and at higher temperatures (above about 550 K) the two processes become difficult to distinguish and the influences of the pressures of all gases present increase. Providing a mechanistic explanation of the complex reactions that contribute to salt breakdown is made more difficult by the unusual (possibly unique) nature of the solid reaction product, which is chemically identical with the reactant. Much effort has been directed towards explaining the restricted extent of this reaction (about 32%) and differences between the reactant and the porous/finely divided, or impure, residual phase, or ‘solid product’.

202 references are cited in Boldyrev’s review [41], including a number of previous reviews. Publications increased in the late 50s and reached a maximum (representing almost a quarter of the articles cited) between 1966 and 1970. After about 1970, fewer papers on the thermal reactions of AP have appeared, but the review is evidence of the continuing interest in, and the remaining unresolved aspects of, the thermal chemistry of this reactant. Boldyrev’s contribution to this field is again considerable, his cited papers providing almost a fifth of those appearing in [41]. His earliest paper on these reactions was dated 1965, the latest 2006.

The mechanism of the low temperature decomposition of NH_4ClO_4

Because reactant and residual product are chemically identical, a novel feedback mechanism is required to account for the observed autolocalization of the low temperature reaction, which is demonstrated by its nucleation-and-growth character. Three possible mechanisms of reactant interaction (electron transfer, anion breakdown and proton transfer) are discussed with reference to the electrical properties of the reactant solid. A review is given of some of the studies that have identified the volatile reaction products, including evidence that the initial breakdown steps yield perchloric acid and ammonia. These may be identified with sublimation but other and/or secondary breakdown processes yield a range of other substances, the most abundant being H_2O, O_2, Cl_2, ClO_2, N_2, N_2O, together with minor quantities of HCl, NOCl, NO_2, etc. Yields vary with temperature and reaction conditions.

Careful microscopic examinations of crystals, including etched faces, during the initiation and development of nuclei have shown that reaction commences in the vicinity of crystal imperfections and the earliest reaction zones are oriented with respect to the reactant crystal lattice. The accumulation of products in sealed, subsurface pores is regarded as resulting in crystal strain, which is capable of inducing deformation that induces new dislocations, sites where further reaction may be started, autolocalization.

After consideration of the alternatives, proton transfer, to yield perchloric acid and ammonia, is identified as the first step in the decomposition, with products accumulating within sub-surface sites of dislocation. The most important participant in salt breakdown is regarded as the chlorate ion, ClO_3^-, which is present as an impurity and acts as a proton trap, breaking down to give ClO_2. Chlorine dioxide is capable of oxidizing ammonium ions to N_2O and ammonia to N_2. The reasons for the incomplete decomposition of the reactant crystal, generating the finely divided NH_4ClO_4 that forms the nuclei, are discussed by consideration of diffusion processes of the participating species (ammonia, perchloric acid, protons) through a detailed model. The account of the factors influencing the balance between concurrent reactions and diffusion processes [41] cannot easily be summarized here, but this interesting and thought-provoking model for reaction demonstrates Boldyrev’s ability to synthesize many diverse observations into a consistent behaviour pattern.

This mechanistic analysis (as with that presented for silver oxalate), includes remarkably few references to reaction rates, activation energy and other kinetic characteristics. However, consideration of the progress made and insights achieved, shows that the fundamental results obtained by a soundly based physiochemical approach have been considerably more successful in elucidating reaction controls than the ‘kinetics only’ method (now widely used [42]). Boldyrev has pointed out that a rate constant measured for an overall reaction is usually a composite quantity (nucleation and growth, different rates of interface advance in different directions, dependence on crystallite sizes, influences of shape, habit, crystal damage, etc.) and does not, therefore, contain detailed mechanistic information. Kinetic theory is regarded as inadequate and is incapable of providing any reliable correlation between apparent activation parameters and the bond redistribution processes involved in solid-state reactions.

The mechanism of the high temperature decomposition of NH_4ClO_4

This reaction is identified [41] as being (similarly) initiated by a proton transfer step, but at crystal surfaces, rather than sub-surface sites, and decomposition proceeds to completion.

Heterophase additives

The numerous published studies of the effects of heterophase additives, including a wide variety of oxides, on the decomposition of ammonium perchlorate are surveyed in [41]. The diverse patterns of behaviour reported in the many published articles mentioned are discussed with reference to the above reaction model. Other sections of this review discuss the role of irradiation in accelerating salt decomposition. The analyses in this [4], as in his other articles, always mention the unfilled gaps in the information available and areas are identified where further work is required to provide deeper insights into the reaction mechanism and controls.

An alternative viewpoint

It is accepted that ammonia and perchloric acid are initial and invariable products formed on heating NH_4ClO_4, this can be identified with the sublimation that always accompanies decomposition. However, Galwey has proposed [43] that the low temperature decomposition reaction is most satisfactorily explained by direct or indirect oxidation of ammonia and/or the NH_4^+ ion to form liquid droplets of nitryl perchlorate, NO_2ClO_4, and, within this molten medium, salt breakdown proceeds preferentially. This is consistent with many of the mechanism proposals in [41] but, in addition, it explains the ability of nitrates to promote AP decomposition [43], and also the following observations. Ammonium nitrate initiates the low temperature reaction across all reactant surfaces. Analytical evidence detected the presence of small amounts of oxidized nitrogen in partially decomposed AP. The proposal that chlorate contributes to nucleation [41] provides support for the participation of the oxidized nitrogen species because the decomposition of ammonium chlorate yields ammonium nitrate [44]. Kinetic comparisons between the rates of decomposition of AP and of NO_2ClO_4 are entirely consistent [43] with the participation of the latter in promoting decomposition of the former. Finally, the restriction of NH_4ClO_4 decomposition to within active and moving molten droplets, that ‘burn holes’ through the reactant crystal, very satisfactorily accounts for the unusual, possibly unique, porous texture of the decomposed salt shown (and discussed) in [43].

Dehydration of copper sulfate hydrates

Copper sulfate pentahydrate was selected [45–47] as a representative reactant to investigate the kinetics and mechanisms of topochemical reactions, recognizing that products may be amorphous or crystalline, intermediate hydrates may be formed and there may be a Smith–Topley effect [5]. These studies demonstrated the value of using X-ray [45], and later synchrotron [16], radiation and crystallographic diffraction methods to characterize product crystal structure and its orientation with respect to the reactant. The reactions were investigated under a range of conditions, including different prevailing pressures of water vapour.

In vacuum, the dehydration of $CuSO_4\cdot 5H_2O$ yielded star (X-) shaped nuclei but, at higher water vapour pressures, elliptic nuclei were formed (the crystalline trihydrate) and the X-shaped nuclei became rounded (the crystalline monohydrate). Crystallographic measurements showed that the *a*- and *b*-axes of the trihydrate are perpendicular and parallel to the (110) direction in the pentahydrate respectively and that the *c*-axes are parallel. Thus the product crystal is oriented with reference to the reactant structure, topotaxy, and the course of reaction greatly depends on the availability of water in the reactant environment.

In 1972, Lyakhov and Boldyrev published a review of the kinetics of dehydration reactions [48].

Comment

A novel dehydration mechanism [49, 50] explains structural water losses from highly hydrated salts, such as alums, by a model in which the essential function of the nucleus is to restrict slightly the ease/rate of water loss. It is believed that a small amount of the product H_2O is retained within the nuclei, at the active reaction interface and remains adsorbed on the hydrophilic reactant. It is envisaged that here it promotes the (difficult) steps that are required for the elimination of the water of crystallization, and the accompanying product recrystallization processes, enabling salt dehydration to propagate (interface advance). This accounts for the autolocalization of reaction within growth nuclei. Dehydration occurs less readily on the dried external crystal faces where propagation of an initial limited superficial water losses rapidly become inhibited because transformation to the structure of the lower hydrate product cannot so readily occur. Exposure of a dehydrated, but unnucleated, superficial layer to water can result in distortion and enhanced ease of subsequent nucleation, attributed to surface strain relaxation.

Thermal decomposition of potassium permanganate

The thermal decomposition of $KMnO_4$ has attracted considerable interest from different research groups over many years [5]. In one of the earliest studies, unusually proposing a mechanistic explanation for a solid-state decomposition, Prout and Tompkins [51] interpreted the observed rate characteristics as evidence that reaction proceeded by a branching chain process. This provided the quantitative model for the kinetic expression that is now frequently referred to as the Prout–Tompkins equation and which continues to be widely used [5] in kinetic and mechanistic studies of crystolysis reactions. Initially, the decomposition of $KMnO_4$ appeared almost as a model reaction, holding hope for similar progress throughout the field. Such optimism was, however, premature and the 'simple' reaction has since been shown to be much more complicated than was appreciated during the early work.

The concept of a solid-state decomposition controlled by 'energy chains' was shown to be inapplicable because, unlike the homogeneous rate processes on which the model was based, such energy would be rapidly dispersed throughout the crystal, rather than specifically transferred to 'trigger' the breakdown of a neighbouring ion or ions. However, this difficulty was overcome by suggesting that reaction was accompanied by reactant crystal cracking and disintegration. Such behaviour was capable of explaining the initial acceleratory reaction observed and it was confirmed [52, 53] that, during the early stages, rates of reaction increase with reactant surface area. However, it was also shown that kinetic characteristics [5] during the acceleratory period vary with sample age [54] and pretreatment. In addition to the Prout–Tompkins equation [51], the decompositions of different samples of this salt were satisfactorily, but alternatively, represented by the power law [55] or the Avrami-Erofeev equation [56]. Again, this multiplicity of kinetic behaviours, shown by different reactant preparations, is entirely consistent with the view (discussed by Boldyrev [11–13]) that the rate equation is not a fundamental, or an invariable, characteristic of the isothermal decomposition of a particular crystalline compound. Interpretation of such data does not yield mechanistic information.

Analytical measurements showed that this reaction is not expressed by a simple stoichiometric equation but was reported [57, 58] as being more satisfactorily represented by:

$$10KMnO_4 \rightarrow 2.6K_2MnO_4 + \text{'}K_4Mn_7O_{16}\text{'} + 6O_2$$

The composition of product '$K_4Mn_7O_{16}$' was approximated to K_xMnO_{2+y}, where x is about 0.5, and it contains potassium intercalated between $(MnO_2)_n$ layers, referred to as the δ-MnO_2 phase. This residual product is a poorly crystallised, perhaps non-stoichiometric, and inhomogeneous mixture of oxides: higher temperatures are required to form recognisable crystalline products [59]. There may also be highly disordered material, perhaps approaching a vitreous or fluid state, present at the reaction interface. The structures and compositions of the residual product, or products, other than K_2MnO_4, remained incompletely characterised.

An early study (1969), by Boldyrev [60], on the decomposition of $KMnO_4$ as a solid solution with $KClO_4$ extended the work of Phillips and Taylor [61]. In dilute $KClO_4$ solid solution, $KMnO_4$ decomposition at 508 K is incomplete, the extent of reaction being related [60] to the proportion of MnO_4^- present in the host lattice as other than isolated units [62]. Groupings of MnO_4^- ions, dimers and more extensive associations, are believed to be necessary to permit decomposition to proceed through an electron transfer step represented as:

$$\begin{array}{ll} 2MnO_4^- \xleftrightarrow{k_1, k_{-1}} & MnO_4^{2-} + MnO_4 \\ & \qquad\qquad \downarrow k_2 \\ & \qquad\qquad MnO_2 + O_2 \end{array}$$

Using a steady-state argument, Boldyrev [60] derived the rate expression:

$$\text{Rate} = k_1k_2[MnO_4^-]/k_{-1}[MnO_4^{2-}] + k_2$$

where $[MnO_4^{2-}]$ is a measure of the number of electrons present in the crystal and $[MnO_4^-]$ is the concentration per unit area of interface.

Significant progress in understanding the stoichiometry of $KMnO_4$ breakdown resulted from the positive identification of $K_3(MnO_4)_2$ in the residual phases during the early stages of reaction [63, 64] by X-ray diffraction measurements. The intensities of peaks for this double salt, a solid intermediate, diminished as reaction continued and the yield of product K_2MnO_4 increased. Erenburg *et al.* [65, 66]

have shown that the decompositions of $RbMnO_4$ and $CsMnO_4$ are different in that manganates are the first products of decomposition, behaviour which is contrasted with the intervention of the crystalline double salt in $KMnO_4$ breakdown. Current opinions on the decomposition of $KMnO_4$ have been critically reviewed by Herbstein *et al.* [67]. They accept the intervention of the double salt as an intermediate and discuss the conclusions that are acceptable, together with problems that remain unresolved.

Additives either catalyze or inhibit $KMnO_4$ decomposition, depending on whether their electronic work function is greater or less than that of the reactant, as has been shown [60] for a range of different MnO_2 preparations. Kabanov and Zharova [68] concluded from conductivity studies in the early stages of decomposition ($\alpha<0.16$) that K_2MnO_4 is formed in solid solution with $KMnO_4$. The double salt, $K_3(MnO_4)_2$, prepared by co-precipitation of $KMnO_4$ and K_2MnO_4, is more stable than $KMnO_4$. Thus MnO_2, one of the solid decomposition products of $KMnO_4$, catalyzes the reaction, while the other, MnO_4^{2-}, is an inhibitor.

Any mechanistic explanation of this reaction must include the intermediate formation of $K_3(MnO_4)_2$ [64] and the predominant overall decomposition includes, therefore, two consecutive rate processes, perhaps:

$$3KMnO_4 \rightarrow K_3(MnO_4)_2 + \delta\text{-}MnO_2 + O_2$$

$$2K_3(MnO_4)_2 \rightarrow 3K_2MnO_4 + \delta\text{-}MnO_2 + O_2$$

together with a possible concurrent contribution from:

$$2KMnO_4 \rightarrow K_2MnO_4 + \delta\text{-}MnO_2 + O_2$$

Complete characterization of the $KMnO_4$ decomposition would require measurements of the variations with time of each of the participating phases. The fit of kinetic data to the Avrami–Erofeev equation (n=2) [59], together with the appearance of nuclei, can be regarded now [67] as only an incomplete representation of this more complicated reaction.

The decomposition of $KMnO_4$ is sensitive to pre-irradiation [69] by UV [70], X-rays, γ-rays, protons and neutrons. The effects increase with dose, decreasing the induction period and increasing the maximum reaction rate, although the changes in kinetic model and the magnitude of E_a are less significant. (Comparable behaviour has been described for other alkali permanganates [65, 66]). There is some controversy about the mechanism whereby irradiation influences reactivity. Prout [69] favoured a displacement model, with multiple ionization of MnO_4 groups leading to formation of random interstitial cations. Boldyrev *et al.* [71, 72] believe that radiolysis products catalyze decomposition. Protashchik and Erofeev [73, 74] take an intermediate view.

Listed E_a values for $KMnO_4$ decomposition are in the range 130 to 210 kJ mol^{-1} but the energy for charge transfer measured spectroscopically [75] was somewhat higher. An X-ray diffraction study [76] of the structure of stoichiometric $KMnO_4{\cdot}K_2MnO_4$ identified discrete MnO_4^- and MnO_4^{2-} ions in the monoclinic cell. It was further shown that there was a high rate of electron transfer, between about 270 and 330 K, with E_a=49±5 kJ mol^{-1}.

The history of characterizing the chemistry of the $KMnO_4$ decomposition emphasizes the care that is essential in formulating a mechanism for a crystolysis reaction by the interpretation of rate data. The smooth, almost symmetrical, sigmoid-shaped yield-time curves for oxygen evolution were accepted unquestioningly [51] as evidence of a simple (i.e., single) rate controlling process, and this 'well-behaved' reaction could be represented by a simple reaction model. It was only later, when the decomposition products were investigated in detail, particularly including the [63, 64] characterization of all participating phases, that the mechanistic complexities were discovered. This is an excellent example of the uncertainty inherent in chemical interpretations of solid-state reactions based only on kinetic observations.

Conclusions

An important principle, maintained throughout Boldyrev's many valuable contributions to the elucidation of the mechanisms of solid-state decompositions, is that the interpretation of kinetic observations yields little (if any) information that is capable of characterizing the detailed chemistry of interface reactions. He has argued strongly and convincingly [11–13] that, unlike homogeneous processes, kinetic parameters determined for heterogeneous reactions proceeding in solids do not contain the essential information from which the molecular steps controlling the change can be deduced. Throughout his extensive work, kinetic observations are discussed, and their significance appreciated, but in considering the controls of a reaction, the reactivity of a solid, it is other physical and chemical measurements that provide the more valuable and the more important insights. He shows that physico-chemical measurements, other than rate, often provide greater and more reliable information concerning the chemistry of the reactions of interest. For example, diffusion processes are demonstrated to be important in many rate processes involving solids. Examples given include interstitial silver ions in silver oxalate breakdown and the initial volatilized products (ammonia and perchloric acid) in ammonium perchlorate decomposition. It is also a feature of many solid-state reactions that the evidence available is insufficient to characterize unambiguously and comprehensively all the steps involved in the conversion of some reactants to products. In his extensive reviews, Boldyrev has mentioned shortcomings in the evidence available and features of the reaction that require further work. For some of the reactants considered above, alternative mechanistic interpretations are given here, exemplifying the difficulties that can arise when formulating a comprehensive model for the thermal decomposition of a crystalline solid.

Despite Boldyrev's clear and extensive demonstrations of the unreliability of conclusions based on the interpretation of kinetic observations alone, this approach to the mechanistic investigation of crystolysis reactions continues to appear in the thermochemical literature. Attention has been drawn to the fundamental limitations inherent in this approach [42], but papers continue to slip by editors and referees. Returning to Boldyrev's metaphor, mentioned above [3], of a desert with few oases, researchers in the field of decomposition of solids can be grateful for the water, food and shade that he has generously provided. As is typical of the field, these resting places have not always marked the ends of journeys, but the refreshment provided has enabled travellers to continue with restored energy and hope.

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