Mechanisms of selected solid state decompositions: Aspects of the interpretation and theoretical explanation of experimental observations

Andrew K Galwey

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

Abstract: The use of kinetic and microscopic observations in the formulation of realistic and meaningful mechanisms for thermal reactions of initially solid compounds is discussed in general and illustrated through references to particular rate processes. The value of using chemical principles to characterize reaction geometry and interface chemistry for reactions proceeding through the advance of an active reactant/product zone is discussed. The possibility that chemical changes in initially crystalline material may proceed with melting is considered through references to systems in which the detection of the liquid phase is difficult. The importance of characterizing the reactant, the products and any intermediates, with references to their chemical properties, is discussed. Trends of behavioural similarities are considered in groups of rate processes involving related reactants. It is concluded that the most reliable theoretical deductions for any reaction are based on complementary types of experimental measurements and observations. Some reactions, formerly regarded as occurring in the solid state, are now identified as involving the essential participation of a liquid or a melt.

INTRODUCTION

I am very conscious of the privilege of presenting a research contribution at this Meeting. I would like to use the occasion to discuss aspects of the role of thermal methods in investigating reaction chemistry. I approach the subject as a chemist and, benefiting from the contributions by my friends in physics, material science and related disciplines, my primary objective is to use all methods available to identify the factors that determine the reactivities of solids. We can expect to advance fundamental chemical theory if we can establish meaningful reaction mechanisms by recognizing intermediates and characterizing the bond redistributions that control the overall rate of change. I will, therefore, direct attention towards investigations concerned with elucidating the chemistry of those steps that determine reactivity when initially solid reactants are heated.

In considering the changes that occur when a reactant that is *initially* a crystalline solid is heated, it is essential to interpret observations with due consideration of the possibility that the material may undergo a loss of structural order at elevated temperature. It is undoubtedly true to say that the first change undergone on heating numerous and diverse solid substances is melting. The melting point has long been recognized as a reliable characteristic feature that may be used to identify compounds.
In contrast, many thermoanalytical studies and investigations of the chemistry of solids direct interest towards the reactions that occur at elevated temperatures. Such work does not, however, always include consideration of the possibility that melting may have occurred where this may be local, temporary or partial within a reacting condensed phase. Such intervention of a fluid is not always easily detected.

The present contribution discusses reaction mechanisms of solids with emphasis on the possible participation of melting and the significance of this phase change in the rate process. The necessity of complementing rate studies with other types of experimental measurements and observations is emphasized with particular stress on the value of microscopic examinations (both optical and electron microscopy). Solid state chemistry possesses the important advantage that it permits reactions to be visually inspected by microscopy. This approach is sometimes, but not invariably, exploited and it must be commended as the most effective and efficient route towards the elucidation of many aspects of the chemistry of solids. It is a truism to state that the greatest insights into the mechanisms and controls of reactions of solids are through the consistent reconciliation of observations from diverse and complementary experimental techniques.

KINETICS OF SOLID STATE REACTIONS (1)

A central tenet in the theory of solid state reaction kinetics is that chemical changes may occur preferentially, or, sometimes exclusively, at a reactant-product interface that progressively advances through the reactant crystal (1). This contact is a zone of locally enhanced reactivity wherein the bond redistribution steps occur most readily. Such locally enhanced reactivity is explained *(inter alia)* by the influence of strain across the lattice discontinuity and/or catalysis by the solid product (1).

The present survey is concerned with the theory developed through interpretation of observations for model systems selected as relatively simple reactions. The theory so established can then extend understanding of more complicated solid state processes.

Two complementary features of interface advance reactions must be individually characterized, though both have not always been investigated (2). Both sets of results are then required to lead to a consistent representation of the overall chemical change. These alternative aspects of behaviour are "Reaction Geometry and Interface Chemistry".

Reaction Geometry

The rate equation fitted by a given reaction provides evidence concerning the systematic changes in the disposition of the advancing interface within the reactant crystal during its progress from initiation to completion. Isothermal sigmoid shaped yield-time curves, for example, are found for nucleation and growth processes. Other deceleratory reactions may proceed by a contracting envelope interface model and there may be diffusion control (1).

Interface Chemistry

Elucidation of the chemical steps occurring within the reaction interface is usually based on indirect evidence. These reaction zones are often very thin, sometimes inaccessible to direct experimental investigation, and the structures may change irreversibly on exposure.

It is useful, therefore, to consider the kinds of information that may be deduced from different types of experimental measurements and discuss how such evidence can be used in the formulation of meaningful reaction mechanisms.

KINETICS. Rate equations (of the form: $f(\alpha) = kt$) may be used to characterize Reaction Geometry. Arrhenius parameters (A and E) may permit deductions to be made concerning the nature of the controlling bond redistribution steps participating in the Interface Chemistry.

STOICHIOMETRY. May provide evidence concerning the essential bond redistributions occurring within the Interface Chemistry.

MICROSCOPY. Often gives direct evidence concerning Reaction Geometry. Textural features may also be helpful in elucidating the Interface Chemistry (Fig. 1).

ENTHALPY CHANGES. Kinetic analyses of heat evolution can be used to characterize the Reaction Geometry. The magnitude of the enthalpy change can be helpful in elucidating the Interface Chemistry. In addition, heat absorption or release can be used to detect reactant phase changes including melting or solidification.

DIFFRACTION. Crystallographic diffraction studies are capable of detecting topotaxy (3,4) that is an important feature in proposing reaction mechanisms and is evidence of the interface structure.

In discussing the detailed mechanisms of interface reactions proceeding between two solid phases, reactant and product, it is worth making the point that reactants and intermediates are immobilized in close proximity. This contrasts with homogeneous rate processes where collisional encounters are necessarily of very brief duration. It follows, therefore, that within active interfaces there are possibilities of mechanistic routes that would not be effective in the gaseous phase or in solution. The following considerations apply.

1. Low or very low concentrations of intermediates may be present, immobilized within a reaction zone that may have a thickness of molecular dimensions.

2. Termolecular collisions, or higher reaction order, may be effective because the participating species are held in close proximity by an effective 'cage'. The prospect of co-operative reactions or interactions, involving several entities, is heightened by a regular or semi-regular structure within the zone of a chemically active interface.

Complementary measurements of different types and interpreted with consistency, are expected to yield the most reliable and theoretically useful representations of reaction mechanisms.

Decompositions and related reactions of solids have been the subject of several extensive reviews, from the early classic survey of the field edited by Garner (5) to more recent publications (1,6). The present communication critically considers the possibility that specific rate processes in this well-established field may be accompanied by melting, which can be local and temporary. For selected thermal decompositions, for example silver malonate (7) and potassium permanganate (8) (see Fig. 1), detailed kinetic and microscopic work has led us to conclude that these proceed without the intervention of melting. We now consider related condensed phase rate processes where there is evidence that a liquid phase plays an essential role in the reaction.
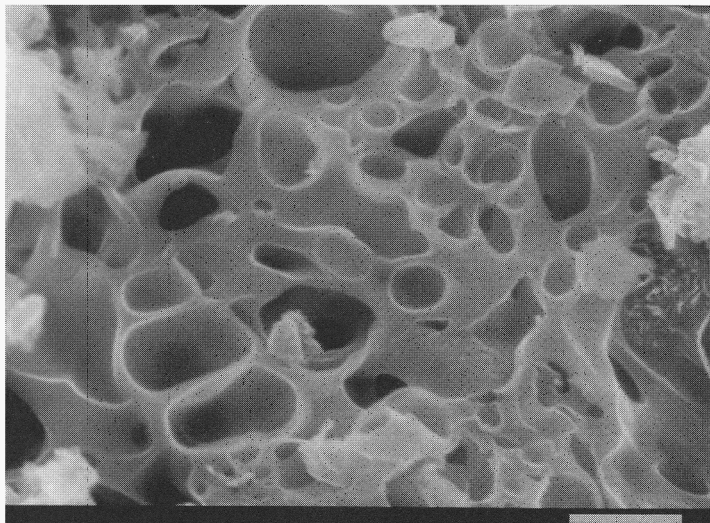
Fig. 1 Crystalline features developed during ($\alpha = 0.1$), the thermal decomposition of potassium permanganate (16). The generation of these complicated intergrown crystals within reactant particle faces would suggest control of reaction by crystallographic factors. There was no evidence of the formation of the characteristic curved surfaces and froth fo§nnation that can be identified with reactions accompanied by melting. Scale bar = 1.0 μm.

MELTING

The solid reactant will become a liquid during a thermal reaction if the melting point is exceeded but also if a eutectic is formed between reactant and a product. There is also the alternative possibility that reactant may be dissolved if a liquid product is retained in or on the reacting solid. The consequent loss of the close and regular intracrystalline environment around the reactant constituents may be accompanied by an increase in their reactivity for the following reasons:
1. The intracrystalline stabilizing forces are relaxed;
2. There is a greater stereochemical freedom for reactants to adopt that reaction precursor configuration that requires the least energy for activation during chemical change;
3. There is increased freedom of interaction between all components of the reactant.

Kinetics of Reactions of Solids with Melting
A range of rate equations is now well-established as being applicable to reactions of solids (1,5,6). However, relatively much less attention has been directed towards considering the kinetic characteristics of those reactions in which there may be melting or in which a liquid phase participates. It is possible in theory that similar, perhaps the same, rate expressions may be capable of accurately expressing the rate data for reactions of both types. If such similarities are demonstrated, then kinetic evidence alone would be insufficient to make the important distinction between solid (only) and solid/liquid reaction mechanisms.

In considering the kinetic characteristics of reactions involving solids in which there is also melt formation, it seems probable that the behaviour will depend on the proportion of liquid present (where the chemical change proceeds in this phase). The following situations can be expected to be of interest.
COMPREHENSIVE FUSION. It might be expected for a solvent-free melt that rate equations, characteristic of homogeneous rate processes, will be applicable, perhaps first or second order behaviour. However, this expectation has not been confirmed in the two systems of this type that we have examined. The rates of dehydration of *meso* and of *dl* lithium potassium tartrate hydrates (9, 10) are represented most satisfactorily by the zero order rate equation and the calculated activation energy values are relatively large. Clearly more work is required to establish trends and patterns of rate characteristics for this type of rate process (a solvent-free liquid).

PROGRESSIVE FUSION. These rate processes are envisaged as proceeding with a progressive increase, throughout reaction, of the amount of liquid phase present in which the chemical change preferentially occurs. Such a reaction can be expected to exhibit a sigmoid shaped fractional reaction (α)-time curve. A kinetic model of this type was proposed to explain the rate characteristics of copper(II) malonate decomposition (11) (Fig. 2) for which the extended acceleratory phase was very satisfactorily expressed by the exponential law. Fusion was ascribed to the formation of copper acetate as an intermediate and the microscopically examined intracrystalline textures gave evidence of froth formation during this liquefaction. Another example of similar behaviour is the decomposition of ammonium dichromate (12) where the molten intermediate was identified as CrO_3 which melts close to the temperature at which the reaction was studied. Again textures observed microscopically confirmed the participation of a molten phase.

INTERFACE FUSION. If liquefaction is confined to a *thin* zone at the reactant-product contact interface, kinetic characteristics will be identical with those of other processes represented by interface advance models (1). The problem in mechanistic investigations is, therefore, to recognize whether there is a liquid layer at the reaction zone. A model of this type may be applicable to alum dehydrations where the function of the nucleus has been identified (13) as water retention. Other nucleation and growth processes for which there is convincing evidence of the participation of liquids are the decomposition of ammonium perchlorate (14) and the reaction of chlorine gas with potassium bromide (15). Detailed discussions of these reaction mechanisms are given in the articles cited.

DETECTION OF MELTING DURING REACTION

In many reactions the detection of partial, local and temporary melting is experimentally difficult. The residual particles from copper(II) malonate decomposition are pseudomorphic with those of the reactant (11), tending to obscure the occurrence of fusion. Evidence that intracrystalline melting has taken place is obtained only by microscopic examination of particle centres. These exhibit a froth-like texture of bubbles having curved surfaces attributed to control by the forces of surface free energy rather than crystallographic factors (Fig. 2). It was concluded that, during the early part of reaction, particle surfaces were modified to unreactive boundaries that retained crystallise individuality and prevented coalescence through sintering. The residual product from ammonium dichromate decomposition was also froth-like and textures resembled those of the solid obtained following the reaction of CrO_3 (the probable decomposition intermediate) with NH_3 (12). The pores generated by reaction in ammonium perchlorate (14) again exhibited characteristically rounded surfaces that were interpreted as evidence for the intervention of a liquid.
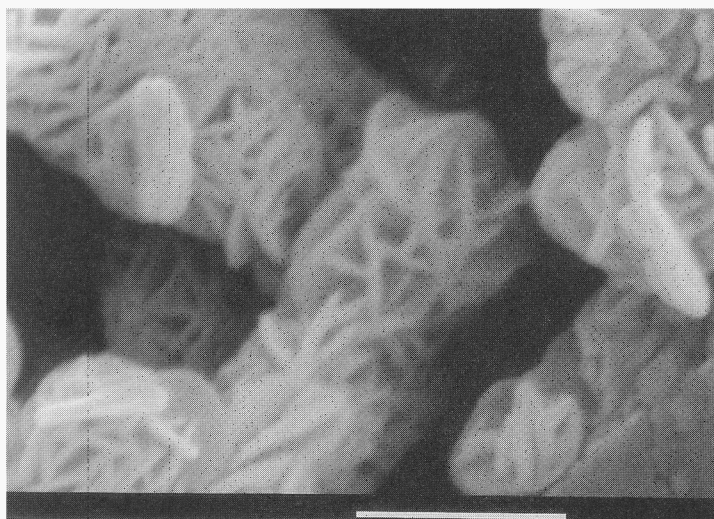

Fig. 2 Intracrystalline froth-like texture revealed on crushing particles of copper(II) malonate after decomposition to ($\alpha = 0.5$ corresponding to completion of the first rate process. The rounded surfaces are attributed to control by surface free energy during evolution of product CO_2 gas in a melt containing copper acetate (11). Scale bar = 1.0 μm.

When reaction and melting occur concurrently and, perhaps, progressively, thermal measurements may not be capable of resolving the contributions from the two distinct processes. As shown by the above examples, the participation of melting can sometimes be identified through the n-microscopic examination of textures. Such studies are most effective when examinations include partially reacted material, as well as the final product, and internal structures are revealed by particle fracture after reaction. Furthermore, evidence of the properties of possible intermediates, most notably the melting point, may be helpful in recognizing melting (12), particularly if there is the possibility of forming a eutectic with the reactant.

MECHANISMS OF SELECTED GROUPS OF RELATED REACTIONS

It was stated in 1980 (p. 11 of ref. 1) that no unifying theoretical concepts had been recognized that were capable of classifying mechanisms and rate controls for reactions of solids. The recognition of trends of behavioural similarities is a necessity in advancing the fundamental theory of the subject. It is important, therefore, to consider, comparatively and critically, the patterns of behaviour discerned within groups of related rate processes. Common features of reaction kinetics and mechanisms are discussed for groups of comparable reactions in the following paragraphs. Such similarities and differences provide some evidence of progress but also illustrate the difficulties inherent in advancing development of this aspect of theory in solid state chemistry.

Thermal Decomposition of Metal Permanganates
The possible role of melting was discussed in comparative studies of the decompositions of $KMnO_4$ (8), $RbMnO_4$ (16) and $CsMnO_4$ (17). All three reactions exhibit sigmoid shaped fractional reaction (α)-time curves and activation energy values were close to 160 kJ mol^{-1}. These significant similarities are ascribed to an identical rate controlling step in all three reactions identified as electron transfer between anions (18). There is an appreciable diminution of decomposition rate ($d\alpha/dt$) at 520 K in the sequence $KMnO_4$ > $RbMnO_4$ > $CsMnO_4$ (16) that is ascribed to the increase in anion spacing in the presence of the larger cations. Kinetic and microscopic evidence supports the view that limited, local and temporary melting occurs during reaction of the caesium salt which was studied within a slightly higher temperature range (17). This contrasts with results for the potassium salt (8) where there is intervention of the intermediate $K_3(MnO_4)_2$ (19) (not formed in the $CsMnO_4$ reaction). Moreover, the formation of a complex crystalline phase during the early reaction (Fig. 1) is evidence of the absence of melting. In all three reactants there is uncertainty regarding the identities of the residual products which may include amorphous and ill-crystallized material (19). This makes the characterization of interface structures difficult. This disorder is, however, consistent with the approach to melting for which there is evidence during decomposition of the caesium salt.
The decompositions of nickel permanganate (20) and of copper(II) permanganate (21) occur at lower temperatures (350-380 K) than the reactions of the alkali permanganates and the calculated activation energies are relatively less (100 and 115 kJ mol^{-1} respectively). Isothermal rate data for both reactions fit the Avrami-Erofe'ev (n = 2) equation (1). Though there was some evidence of sintering during reaction, microscopic information concerning the possible participation of fusion was inconclusive.

Thermal Decomposition of Copper(II) Salts of Organic Acids
A common feature of the thermal reactions of the copper(II) salts of oxalic, malonic, maleic, fumaric, mellitic and of squaric acids was that decompositions proceeded to completion in two distinct rate processes involving the stepwise reduction of the cation, $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$. Kinetic data were summarized in Table I of ref. (22) and more detailed reports of each of these reactions are given by the references cited therein. Positive evidence of melt formation was obtained only for the reactions of copper(II) malonate (Fig. 2) and copper(II) maleate. There were no indications of fusion during the decompositions of the other salts, though this may have been due to insufficient microscopic resolution. It is clear that copper metal was not an early product of reaction and, because this product (metallic Cu) does not promote anion breakdown, decomposition does not proceed by a metal catalysed nucleation and growth mechanism. Later in the reaction, however, product metal exhibits sufficient mobility to aggregate as small crystals (11), showing its ability to migrate across the other residual phase, a carbonaceous material.

Dehydrations of Lithium Potassium Tartrate Hydrates
Kinetic studies of the dehydrations of these salts were undertaken to compare reactivities of solids composed of identical constituents but in which the *d, dl* and *meso* forms of the anions crystallize with different structures. The patterns of water elimination rates for the three reactants showed unexpectedly large differences (23).
d $LiKC_4H_4O_6 \cdot H_2O$ (24). Below 460 K this dehydration proceeds by a nucleation and growth mechanism characteristic of many solid state rate processes. The fractional reaction-time curve is sigmoid shaped and the Arrhenius parameters are $E = 160$ kJ mol^{-1} and $A = ca.$ 10^{16} sec^{-1}. Above 460 K the mechanism changed, apparently due to reactant melting, and the Arrhenius parameters were substantially increased ($E = 350$ kJ mol^{-1} and $A = ca.$ 10^{38} sec^{-1}).

dl (racemic) $LiKC_4H_4O_6 \cdot H_2O$ (10). This compound melted during dehydration and subsequent water evolution proceeded by an approximately zero order process with large apparent values of E (= 330 kJ mol^{-1}) and A (= *ca.* 10^{35} sec^{-1}).

meso $LiKC_4H_4O_6 \cdot 2H_2O$ (9) melted during dehydration and, like the *dl* isomer, approximately obeyed the zero order equation with E = 230 kJ mol^{-1} and A = *ca.* 10^{30} sec^{-1}.

Magnitude of Activation Energy Values for Decompositions of Transition Metal Salts of Carboxylates

A trend has been discerned between the magnitude of the activation energies for the decompositions of transition metal oxalates and mellitates and the heats of formation of the metal oxides (25,26). From this it was concluded that rupture of the bond between cation and carboxylate oxygen is probably a controlling factor in salt breakdown.

COMMENT

In this survey of selected reactions of solids, the importance of obtaining different types of evidence through the use of complementary experimental techniques in the formulation of reaction mechanisms is emphasized. Reaction models based on deductions from varied types of observation are likely to provide a more realistic representation of behaviour. In particular, we emphasize the importance of establishing whether or not there is participation of melting because this is an essential feature of any fundamental and realistic description of a chemical change. The possibility that there has been melting is not always investigated or explicitly discussed (2). The value of considering the behaviour for a particular solid with reference to the known characteristics of related reactions is illustrated here through mentions of some trends recently reported. The article draws attention to the necessity of including phase changes and *chemical* considerations when developing the theory of thermal reactions and reactivities of initially crystalline reactants.

REFERENCES

1. M.E. Brown, D. Dollimore and A.K. Galwey, *Comprehensive Chemical Kinetics*, vol. 22, Elsevier, Amsterdam, (1980).
2. N.J. Carr and A.K. Galwey, *Thermochim. Acta*, **79**, 323 (1984).
3. H.R. Oswald, *Thermal Analysis, Proc. 6th Internat. Conf. Bayreuth, July 1980*, Birkhaüser, Basel, **1**, 1 (1980).
4. V.V. Boldyrev, *React. Solids*, **8**, 231 (1990).
5. W.E. Garner (ed.), *Chemistry of the SolidState*, Butterworth, London, (1955).
6. J. Sestak, *Thermophysical Properties of Solids, Thermal Analysis*, vol. 12, Part D, Elsevier, Amsterdam, (1984).
7. A.K. Galwey and M.A. Mohamed, *J Chem. Soc., Faraday Trans. I*, **81**, 2503 (1985).
8. M.E. Brown, A.K. Galwey, M.A. Mohamed and H. Tanaka, *Thermochim. Acta*, **235**, 255 (1994).
9. A.K. Galwey, G. M. Laverty, V.B. Okhotnikov and J. O'Neill, *J Thermal Anal.*, **38**, 421 (1992).
10. S.D. Bhattamisra, G.M. Laverty, N.A. Baranov, V.B. Okhotnikov and A.K. Galwey, *Phil. Trans. R. Soc. London*, **A341**, 479 (1992).
11. N.J. Carr and A.K. Galwey, *Proc. R. Soc. London*, **A404**, 101 (1986).
12. A.K. Galwey, L. Pöppl and S. Rajam, *J Chem. Soc., Faraday Trans. I*, **79**, 2143 (1983).
13. A.K. Galwey, R. Spinicci and G.G.T. Guarini, *Proc. R. Soc. London*, **A378**, 477 (1981).
14. A.K. Galwey and M.A. Mohamed, *Proc. R. Soc. London*, **A396**, 425 (1984).
15. A.K. Galwey and L. Pöppl, *Phil. Trans. R. Soc. London*, **A311**, 159 (1984).
16. A. K Galwey, S.A. Lyle and S.A.A. Mansour, *Thermochim Acta*, **235**, 239 (1994).
17. A.K. Galwey and S.A.A. Mansour, *Thermochim. Acta*, **228**, 379 (1993).
18. V. V. Boldyrev, *J Phys. Chem. Solids*, **30**, 1215 (1969).
19. F.H. Herbstein, M. Kapon and A. Weissman, *J Thermal Anal.*, **41**, 3 03 (1994).
20. A.K. Galwey, S.A.A. Fakiha and K.M. Abd El-Salaam, *Thermochim. Acta*, **206**, 297 (1992).
21. A.K. Galwey, S.A.A. Fakiha and K.M. Abd El-Salaam, *Thermochim. Acta*, **239**, 225 (1994).
22. A.K. Galwey and M.A. Mohamed, *Thermochim. Acta*, **239**, 211 (1994).
23. N.A. Baranov, V.B. Okhotnikov, L.I. Rynskaya, A.R. Semenov, A.K. Galwey and G.M. Laverty, *Solid State Ionics*, **43**, 37 (1990).
24. A.K. Galwey, G.M. Laverty, N.A. Baranov and V.B. Okhotnikov, *Phil. Trans. R. Soc. London*, **A347**, 139, 157 (1994).
25. R.J. Acheson and A.K. Galwey, *J Chem. Soc. A*, 1167 (1967).
26. M.A. Mohamed and A.K. Galwey, *Thermochim. Acta*, **213**, 269 (1993); **217**, 263 (1993).