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Crystal chemistry and molecular mechanisms in molten magmas: the significance of fusion in reactions of solids [☆]

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Abstract

The possible role of melting in thermal reactions of initially solid reactants is not always explicitly considered in the interpretation of kinetic data and the formulation of reaction mechanisms. The present paper discusses reasons for the enhancement of reactivity on fusion and contrasts the rate characteristics of heterogeneous (solid state) with homogeneous reactions. The value of complementing kinetic measurements with analytical data and microscopic textural observations is discussed. The importance of this approach in elucidating meaningful reaction mechanisms is illustrated by considering features of selected kinetic studies of reactions in which it was demonstrated that there was the essential participation of perhaps local and temporary fusion or liquid intermediate formation during chemical changes that had initially appeared to proceed in the solid state. Literature examples are discussed in the text.

Keywords: Crystal; Fusion; Magma; Melt

1. Introduction

Whether or not a solid reactant undergoes melting during a chemical change is a fundamental and essential consideration in the formulation of a reaction mechnism. There are, however, often problems in demonstrating unambiguously that fusion does or does not occur, in reactions involving initially solid reactants. As will be shown in the examples given below, isothermal yield–time data for a number of reactions proceeding

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with the experimentally identified participation of a liquid phase are sigmoid-shaped. These measurements are sometimes well represented by those rate equations which have been developed for quite different reaction models, such as nucleation and growth process, that proceed in the solid state [1]. We here discuss the kinetic characteristics of reactions in which the chemical changes are accompanied by the appearance of mixed reactant phases, including solids, but accompanied by local and/or temporary fusion. We regard this possibility as an essential consideration in the general theoretical rate analysis of condensed phase reactions. This important aspect of the kinetic interpretation of the behaviour of initially crystalline solids, or of solvent-free liquid reactants, has not been developed as generally as it merits. The incorporation of such reaction models into our kinetic analyses is important to widen insights into and understanding of the chemical controls on reactivity and we believe that the results are of interest to solid state kineticists. This feature of condensed-phase chemistry is regarded as relevant to the field of thermal analysis where numerous studies of the thermal process occurring in initially solid reactants have been reported: the concepts and interpretations discussed here should be useful in the formulation of meaningful and realistic reaction mechanisms.

2. Mechanisms of homogeneous and of heterogeneous reactions

The reaction mechanism is the sequence of chemical steps through which reactants are converted into products and includes the characterization of the role of any participating intermediates and should also recognise the significance of any catalyst or phase change. Mechanisms are usually elucidated by kinetic measurements. Results are of value in extending our theoretical understanding of the factors that control reactivity and may also find applications in designing preparative or manufacturing processes.

2.1. *Homogeneous reactions*

Rates of reactions occurring in the gas phase or in solution are frequently controlled by the *concentrations* of the participating species and are thus characterized as first or second order and interpreted as unimolecular, bimolecular, etc. In chain reactions, a sequence of interlinked, chemically simple, contributory steps can be identified or, more usually, deduced from appropriate kinetic measurements. This important area of physical chemistry is well established, successful and contributes to our theory of chemical reactivity often through the transition state theory, which provides a unified theoretical foundation for the comparative consideration of the properties of related chemical systems.

2.2. *Heterogeneous reactions*

Chemical changes proceeding in crystalline reactants differ (from those referred to above) in that reactions often occur at interfaces [1]. Such interfaces may be a reactant–

product contact that advances progressively into the unchanged material, as in nucleation and growth processes, or a contact at which chemical changes occur after diffusion of species across an assemblage of solid product material situated between the reactants, as in corrosion reactions. Rate equations specifically applied to the reactions of solids [1] usually include a term expressing quantitatively the systematic changes in geometry of interface development (area) as reaction progresses and do not include concentration terms. There is no final agreement about the significance of Arrhenius parameters for solid state reactions [1].

2.3. Melting during reaction

The alternative kinetic characteristics of homogeneous and of heterogeneous reactions referred to above are discussed extensively, but separately, in the literature. We mention these contrasting types of behaviour here only as an essential background for our consideration of reaction kinetics in reactant systems containing both solid and liquid phases. The latter may arise through formation of a low melting point intermediate, product or eutectic and fusion may be local and/or temporary. Such mixed-phase reactant systems appear to have been the subject of little interest, investigation or discussion. We consider below the interpretation of measured kinetic data for reactions in which there is the essential intervention of melting or the formation of a eutectic or of a liquid intermediate. The experimental investigation of such processes can be made more difficult by the problems that are sometimes encountered in establishing unambiguously whether or not there has been the local or temporary intervention of a melt. This is important because there is evidence that, in general, chemical processes proceed more rapidly in the homogeneous phase than in crystals, as discussed below.

3. Relative reactivities of crystals and fluids

Experimental results, together with theoretical justifications [2], have led to the view that reactions proceed more rapidly in a melt than in a crystalline solid. Such a conclusion is difficult to demonstrate generally but it is a useful concept that is consistent with the evidence discussed here in support of the view that some chemical changes proceed preferentially in a liquid or a fused or amorphous, disorganized state. Theoretical reasons are as follows.

1. Crystal packing stabilizes lattice constituents

Intracrystalline attractive forces between lattice components (ions or molecules) confine bond vibrational movements, thereby stabilizing lattice components, so that reactivity is relatively reduced in the crystalline state.

2. Stereochemical constraints oppose attainment of the most favourable pre-reaction configuration

The close proximity of neighbouring components in the crystal may oppose the adoption of that reactant configuration which represents the route providing the lowest energy barrier to chemical change. Thus reaction in the solid must proceed either through a less efficient pathway or with the cooperative movements of other crystal components.

3. *Restriction of interactions between specific components of the reactant entities*

Reactant immobilization in specific orientations within the crystal may inhibit or prevent the interactions between the particular bonds of different participating ions or molecules. This can be expected to be of greater significance in reactants containing larger components.

4. *Immobilization of reaction promoters within the solid*

The promotion of reaction by products (autocatalysis) (also impurities) or by a lattice component such as water of crystallization can be inhibited if such species are immobilized within the reactant crystal.

Reaction may, therefore, proceed more rapidly in a melt because the stabilizing forces of coherence within the crystal are relaxed and/or because there is freedom to adopt the most favourable reaction configuration and/or to make effective encounters between reactant species. However, there are also conditions in which the properties of crystalline solids enhance reactivity.

1. *Interface strain*

Within the zone of solid-reactant–solid-product contact, the interface of juxtaposition of two different crystal structures is a localized area of strain [3]. Bond redistributions may preferentially occur here because of a local reduction in the energy barrier to chemical change. Reaction proceeds in an ordered zone between two solids.

2. *Interface catalysis*

If the surface of a crystalline reaction product exerts a specific catalytic promotion of a chemical change, comparable to an active heterogeneous catalytic surface [4], the interface chemical change may occur exclusively on the product without melting.

3. *Structure recrystallization*

The reactivity of a solid may undergo an appreciable increase at temperatures in the immediate vicinity of a phase transformation [5]. This has been ascribed to structural instability of the lattice components and is believed to be capable of giving information of value in the elucidation of reaction mechanisms. It has also, however, been concluded [6] that this effect is not real but arises as a consequence of liquid phase formation.

4. *Restricted reaction*

Begg et al. [7] have shown that sodium chlorate crystals undergo a small amount of decomposition in the solid state (0.1–1% mass loss) between 450 K and approx. 535 K, the melting point. The amount of reaction is least for the most perfect reactant crystals and is associated with crystal imperfections, i.e., zones of strain.

4. Interpretation of kinetic data

4.1. Solid state reactions

Reactions are usually envisaged as occurring exclusively at an active reactant–product interface that progressively advances into the unchanged reactant. A mechanistic description of this behaviour requires the consideration of at least the following features of reaction, which must also be reconciled with the kinetic rate expression.

4.1.1. Nature of the interface

During decompositions of many solids, well-established interfaces advance at constant rate [1]. Reactions between solids, or a gas and a solid, result in product deposition between the reactant particles so that rates of interface progress are determined by the rates of transport of appropriate entities across this effective barrier layer.

4.1.2. Interface geometry

The total area of active interface, identified as a measure of reaction rate, undergoes systematic changes as reaction proceeds and due allowance for this controlling parameter must be incorporated into the rate equation [1]. Geometric interpretation of rate behaviour is often usefully supported by microscopic observations.

4.1.3. Interface chemistry

The Arrhenius parameters, activation energy (E) and reaction frequency factor (A), are believed to be determined by the chemical changes occurring at the reaction interface. The significance of these parameters in reactions of solids is by no means generally agreed [1]. It has been suggested [8] that the energy distribution function for crystal components differs from that applicable to assemblages of gaseous molecules and the meaning of both the activation energy and the frequency factor in reactions of solids is not clear. Some workers [1, 8] consider it probable that the controls determining the magnitudes of A and E differ fundamentally from those applicable to homogeneous reactions that are considered theoretically by the transition state theory.

4.2. Homogeneous reactions

Rates of these reactions are frequently proportional to the concentrations of one or more reactants and these terms determine the form of the yield–time relationship. When a solid melts comprehensively prior to the start of reaction, kinetic behaviour may be subject to the same controls as other homogeneous reactions. The study of reactions in solvent-free melts does not, however, appear to have been investigated extensively and examples of such behaviour are mentioned below.

5. Partial melting during reaction

Because such reactions are often complex, and may involve more than a single step or reaction pathway [9], measurements of overall kinetic behaviour may not provide sufficient information to enable the controls of individual reactions to be identified. The complementary data necessary to characterize kinetic behaviour fully may require a number of alternative approaches, including the following.

Kinetic measurements of the generation rates of suitably selected products, each of which may be formed by different pathways may be used [9]. **Thermal measurements** may be used to complement product yield data and, in favourable systems, the occurrence of melting and solidification may be detectable. **Analytical measurements** of the components of the residual materials at known extents of reaction may be used to identify essential intermediates, or products, and to determine their concentration variations as reaction proceeds. Such data may enable their individual roles in the overall process to be identified. **Electron microscopic examinations** may be used to establish the occurrence of melting (or, indeed the absence of melting [10]), and possibly the progressive changes of amount and disposition of liquid material within the reactant as reaction advances. Interpretation of photomicrographs must be completed with care because local melting is not always easily identified.

On heating, a solid may melt comprehensively; such behaviour includes dissolution in water of crystallization, though this may depend on whether or not the water present is rapidly evaporated from the reactant. Other changes leading to liquid formation include the following.

Molten intermediate

An intermediate may be formed that is itself a liquid or that may form a eutectic with the reactant [11] and subsequent chemical changes proceed preferentially in the fused material; e.g. copper(II) malonate, ammonium dichromate and ammonium perchlorate, see below.

Liquid product

A liquid product may dissolve, or form a eutectic with, the reactant and reaction may proceed preferentially in the molten material; e.g. the $KBr + Cl_2$ reaction, see below.

A complete mechanistic description of the overall reaction requires the identification of all significant intermediates and their rates of generation and removal in the context of the kinetics of reactant consumption and principal product formation [9]. In the systems we have examined, described below, it has been found to be experimentally difficult to estimate the amounts of liquid present at various stages of reaction, particularly where melting is local and/or temporary with a spatial distribution within the reactant assemblage that changes as reaction proceeds (see also Ref. [12]). If melting is intracrystalline, the identities of the original individual crystallites of the reactant may be maintained throughout reaction. The development of melt zones, possibly analogous to nuclei in solid state reactions, cannot be quantitatively measured during the course of a reaction, but may lead to kinetic characteristics similar to those familiar from and applicable to decompositions of solids [1].

5.1. Detection of melt formation

Observation

Comprehensive melt formation can be recognized easily [13] where the solid forms a single coherent melted aggregate and often adheres to the reaction vessel.

Thermal methods

A melting endotherm or solidification exotherm [14] can be identified from thermal measurements if it is a separate event, resolved from other responses. Berg et al. [15] used DTA in conjunction with electrical conductivity measurements to identify melting and eutectic formation in reactions of $BaCl_2$ with alkali sulphates.

Kinetic data

The absence of any change in rate characteristics after pre-crushing or pre-irradiation [16] of reactant crystals *may* be evidence of an intracrystalline reaction, independent of surface area, or of fusion.

Properties of intermediates

The positive identification of intermediates known to be molten at or near reaction temperature can be an indication of the probable occurrence of fusion [17].

Microscopic textures

The intracrystalline generation of bubbles or of froth-like appearances, structures consisting exclusively of rounded surfaces where textures are controlled by surface free energy forces [18], is evidence of the participation of a liquid in the chemical change.

X-ray crystallography

This technique can be used to measure quantitatively the amounts of crystalline phases present during high temperature reactions and, by difference, amounts of the non-crystalline material present can be estimated.

6. Reactions with fusion/liquid participation

The reactions discussed here proceed with melting or liquid formation but nevertheless exhibit features usually regarded as being characteristic of solid state processes, such as the form of the rate equation obeyed or the production of residual solid particles pseudomorphic with those of the reactant (evidence that comprehensive fusion has not occurred). Most of these examples have been implicitly identified in previous reports as solid state processes. The studies mentioned here, however, show that there is (what we would accept as) conclusive evidence that a liquid has participated in the chemical change. Each short account is necessarily restricted to a few significant aspects of the reaction described: more comprehensive explanations of the confirmation that a liquid is an essential participant in the process described are given in the references.

6.1. $(NH_4)_2Cr_2O_7$ decomposition: melting of an intermediate, CrO_3 [19]

$(NH_4)_2Cr_2O_7$ decomposition, formerly described and discussed as a nucleation and growth process [20] proceeding in a crystal, has more recently been shown to involve melting, identified by the generation of an internal forth-like texture together with surface bubbles. Yield–time curves were initially sigmoid-shaped, later followed by a linear slower reaction leading to the final deceleration. It is concluded that the overall decomposition involves two principal and certainly overlapping reactions. Dissociation, probably reversible

$$(NH_4)_2Cr_2O_7 \rightleftharpoons 2NH_3 + H_2O + 2CrO_3$$

is followed by ammonia oxidation by molten CrO_3 to yield the principal products N_2O, N_2, H_2O and Cr_2O_3. CrO_3 melts at the lower end of the temperature interval studied. The texture of the residue from the $CrO_3 + NH_3$ reaction was closely similar to that obtained from salt decomposition. This reaction mechanism makes it essential to complement overall kinetic mesurements with analytical data enabling the contributory processes to be individually characterized (salt dissociation, intermediate production: CrO_3, NO_2^-, NO_3^-, etc.) to describe quantitatively the reactions contributing.

6.2. NH_4ClO_4 decomposition: molten intermediate, NO_2ClO_4[21,22]

Previous mechanistic explanations of the nucleation and growth, low-temperature, incomplete (28%) decomposition of NH_4ClO_4 have identified the overall reaction as proceeding with control through electron or proton transfer steps [23], neither of which was finally accepted as satisfactory. Analytical detection of oxidized nitrogeneous species in partly reacted salt, together with the observation that nitrates promote salt decomposition, lead us to conclude that reaction involves the intermediate production of NO_2ClO_4 (NH_4^+ ammonium is oxidized to NO_2^+) which is molten and unstable at the reaction temperature. Reaction is envisaged as proceeding in the mobile and highly reactive fluid droplets of nitryl perchlorate that advance into the reactant crystal.

6.3. Copper(II) malonate decomposition: molten intermediate copper acetate [24]

Yield–time curves for the isothermal decomposition of copper(II) malonate are an unsymmetrical sigmoid shape. The initially acceleratory process is expressed by the exponential law to almost 50% reaction before the rate is markedly reduced in the second rate process, which is first order. These stages were shown by analytical measurements to involve stepwise reduction of the cation ($Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$). The first step was accompanied by acetate formation and resulted in melting. Decomposition generated froth within regions explaining obedience to the exponential rate law, $(da/dt) = ka$ [1].

Crystals of partly reacted salt ($a < 0.5$) remained pseudomorphic with those of reactant, though surfaces were distorted by superficial bubble formation and interiors contained regions of froth. It appears that early reactions modify crystal faces and this preserves the appearances and individuality of crystallites. The identification of intracrystalline melting requires, therefore, the fracture of crystals and microscopic examinations of internal surfaces so revealed. Melting here was shown [14] to overlap with reaction and the expected endotherm could not be detected by DSC, though solidfication was.

Somewhat similar behaviour was shown by copper(II) maleate [25]. Even greater intermediate mobility was detected in the decomposition of copper(II) formate where there is participation of a **volatile** intermediate, probably copper(I) formate [26].

6.4. *Nickel acetate decomposition: possibility of melting [27]*

The kinetic data were regarded as consistent with the intervention of melting during nickel acetate decomposition but this could not be confirmed (or excluded) by electron microscopy and remains unproven.

6.5. *Reaction $KBr + Cl_2 \rightarrow KCl + ClBr$: liquid product, Br_2 [28]*

This reaction, proceeding readily at ambient temperatures, was easily identified as a nucleation and growth process progressing through the development of large orange-coloured nuclei. The observations suggests bromine retention within the product KCl assemblages (nuclei) and reaction ceased when conditions were modified to cause product liquid vaporization, e.g. by evacuation or heating (to 373 K). It was concluded that reaction proceeded in the intranuclear liquid phase $[Br_2]$ by an ionic mechanism

$$KBr \rightleftharpoons K^+ + Br^-$$

$$Br^- + Cl_2 \rightleftharpoons [BrCl_2]^- \rightleftharpoons Cl^- + BrCl(\rightarrow 0.5Br_2 + 0.5Cl_2)$$

$$K^+ + Cl^- \rightleftharpoons KCl$$

The assemblages of small product KCl crystallites, oriented within the nucleus, were permeated by a well developed system of channels. This participation of intranuclear liquid was supported by the observation that nucleation was substantially accelerated by the *liquid* catalyst $SnCl_4$.

7. Conclusions

We believe that chemical changes proceeding in condensed reactant phases, originally solid materials, involve, much more frequently than has been recognized generally, the intervention of a fused/molten or liquid reaction medium, perhaps temporarily and locally. As illustrated in the above examples, evidence indicative of the participation of homogenous reactions can be detected by suitable examinations of samples of partly reacted salt. Kinetic analyses can be complemented through microscopic observations and further supported with thermal and analytical measurements. Confirmation that there has been melting is not always straightforward but the enhanced reactivity associated with loss of crystalline order can be an important consideration in the formulation of a meaningful reaction mechanism.

The above examples are cited here as providing the most reliable instances of fusion. We have also found evidence of superficial melting [29] and the participation of water in the interfacial reaction during dehydration [30]. Dehydration [31, 32] and decomposition [33] of lithium potassium tartrate salts proceed with comprehensive melting; kinetic characteristics are discussed in the references cited.

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