

SOLID STATE DECOMPOSITIONS: THE INTERPRETATION OF KINETIC AND MICROSCOPIC DATA AND THE FORMULATION OF A REACTION MECHANISM *

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ABSTRACT

This article discusses current theoretical concepts that relate to the role of interfaces in reactions involving solids. It is emphasized that the isothermal kinetic characteristics of such reactions are often determined by the progressive changes of interface geometry as reaction advances, and that obedience to a particular rate equation does not necessarily provide information concerning the chemistry of the processes involved. Evidence concerning reactant and product textures and the conditions prevailing at an interface can, in suitable systems, be deduced from microscopic examination of the reactant–product contact zone. Observations of this type have been used to develop a classification scheme for nucleus functions in various reactions. The value of this general approach, the separate and complementary consideration of reaction geometry and interface chemistry in formulating reaction mechanisms, is discussed with reference to the following rate processes: alum dehydrations, the reaction $\text{KBr} + \text{Cl}_2 \rightarrow \text{KCl} + \text{BrCl}$, the decompositions of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, copper malonate, and other metal carboxylates. It is concluded that modern methods of microscopic examination afford a direct and powerful technique for the characterization of the interfacial chemical changes that occur during reactions of solids.

INTRODUCTION

The rates of homogeneous reactions, proceeding in solution or in the gas phase, are controlled by the collision frequencies between the participating molecules and the energy and entropy barriers to chemical change. Thus, from the quantitative measurement of the relationship between the rate of product formation and the reactant concentration it is often possible to determine the molecularity of the rate-limiting step and to characterize other features of the molecular interactions and the reaction mechanism such as, for example, the occurrence of a chain reaction. This approach to kinetic analysis is not, however, applicable to decomposition reactions of solids,

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because the term "concentration" cannot usually be applied to crystalline reactants. Moreover, many such reactions are regarded as taking place exclusively within a specialized zone of locally enhanced reactivity, at the reactant/product contact, the reaction interface [1]. During the transformation of a solid reactant into products, systematic changes in rate result from the progressive variations in total area of this interface as it advances into the reactant crystal.

Conditions prevailing within this moving active interfacial zone are regarded as constant: the contributory chemical changes proceed at a constant rate. It follows, therefore, that product yield–time data cannot give evidence of the molecularity, or other aspects of the mechanism of the controlling bond redistribution step within the advancing interface. Accordingly, a different approach is required in the interpretation of kinetic data for homogeneous reactions and for decompositions of solids, and these fundamentally different types of behaviour must be considered critically during the formulation of mechanisms for reactions involving solids. This point requires emphasis here because the theories and concepts developed in the larger field of homogeneous kinetics have often been uncritically accepted as possessing general applicability.

From a consideration of published discussions concerned with the decomposition kinetics of solid reactants, we identify two features that require both separate and complementary examination during the formulation of a reaction mechanism: the reaction geometry and the interface chemistry [2]. Individual enquiry into these different aspects of behaviour ensures that both components are considered in the context of accepted theory and related reactions. Conclusions reached must also be consistent with each other, since these present alternative perspectives for the same overall chemical change. This point is emphasized here because it has been recently revealed by a literature content analysis [3] that many of the mechanistic discussions appearing in a representative sample set of articles (those concerned with a decomposition reaction of a solid appearing in 1981) did not extend to the elucidation of both aspects of behaviour. Many authors of papers in this survey confined their discussion either to the geometric features of interface development or to the identification of the rate-controlling bond-rupture step.

The present contribution discusses the interpretation of isothermal reaction kinetics under the headings: reaction geometry and interface chemistry. These sections are followed by a short comment on the interpretation of non-isothermal rate measurements with reference to the recent literature. The final section discusses the mechanistic conclusions reached from a number of individual kinetic studies interpreted according to the principles described in the theoretical sections. (Accounts given here for each of these salts are brief, there are more extensive reports in the literature references cited.)

REACTION GEOMETRY

It is usually accepted that solid decompositions are initiated at specialized surface sites. Each nucleation process generates a zone of active reaction interface that advances thereafter into the unreacted material comprising one side of the contact. The number of sites capable of yielding an active nucleus is often limited. For many solid decompositions the nucleation step is regarded as requiring high energy and occurs at specific surface imperfection structures.

Nucleation

Rates of nucleation have been measured by microscopic observations and the following kinetic expressions have found general acceptance (more detailed derivations have been given elsewhere [1]).

Instantaneous nucleation ($N = N_0$, soon after $t = 0$)

Linear nucleation ($N = kt$)

Exponential nucleation ($N = N_0 [1 - \exp(-kt)]$)

Power law nucleation ($N = [kt]^\beta$)

where N is the number of active nuclei present at time t , N_0 is the number of potential nucleation sites and β the number of steps required for nucleus generation.

Growth

Once established, the interface advances at a constant rate [r (nucleus radius) = kt] into the unchanged reactant. The initial rate of growth is sometimes slower than that ultimately achieved and the rate of linear advance may not be equal in all crystallographic directions. The limits to development of nuclei are also subject to constraints imposed by the sizes and shapes of the reactant particles, and also by the relative dispositions and numbers of the other nuclei growing concurrently, since interface advance necessarily ceases when nuclei meet by coalescence.

Nucleation and growth

The extent of a nucleation and growth reaction at time t is sometimes represented by a generalized mathematical relationship (see ref. 1, p. 49), a simplified form of which can be expressed as follows

$$\alpha = \int_0^t \left[\begin{array}{c} \text{nucleation} \\ \text{law} \end{array} \right] \rightarrow [\text{growth}]^\lambda dt$$

Here the fractional decomposition, α , is expressed as the summation of the growth, in λ dimensions, of all nuclei which have been formed at different times during the progress of reaction.

This expression cannot be generally integrated and further difficulties are introduced with consideration of the necessary allowances for shapes and sizes of reactant particles, overlap of nuclei during growth, ingestion of potential nucleus-forming sites into growth nuclei, etc. However, simplifica-

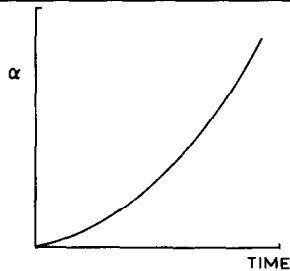
TABLE 1

The kinetic expressions most frequently applied in rate studies of solid-state decomposition reactions

Acceleratory equations

Power law: $\alpha = (kt)^n$, $n = \beta + \lambda$

Exponential law: $\ln \alpha = kt$



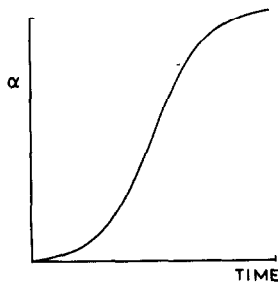
Sigmoid-shaped equations

Avrami-Erofeev equation:

$-\ln(1 - \alpha) = (kt)^n$, $n = \beta + \lambda$

Prout-Tompkins equation:

$\ln[\alpha/(1 - \alpha)] = kt$



Deceleratory equations

Contracting area ($n = 2$) or volume ($n = 3$):

$1 - (1 - \alpha)^{1/n} = kt$

Reaction order:

first order: $-\ln(1 - \alpha) = kt$

second order: $(1 - \alpha)^{-1} = kt$ (empirical)

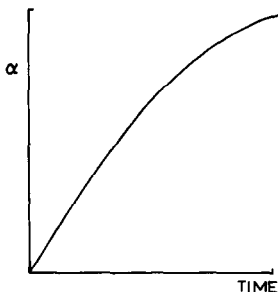


TABLE 2

Testing of kinetic obedience to a rate equation

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- 1 Linearity of calculated $f(\alpha)$ values plotted against time
 - 2 Plot of α against reduced (dimensionless) time and comparison with tabulated data [4]
 - 3 Comparison of reaction rates ($d\alpha/dt$) plotted against α with tabulated data [4]
 - 4 Comparison of reaction rates ($d\alpha/dt$) plotted against reduced time with tabulated data [5]
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Differential methods (3 and 4) require very accurate rate data.

The distinguishability of kinetic models for solid-state decompositions has been discussed [6]. Geometric conclusions from kinetic analyses should, where possible, be confirmed by microscopic observations.

tions are possible and integrations of appropriate less complicated expressions have yielded a limited number of comparatively simple kinetic equations that are accepted as satisfactorily expressing the rate behaviour most frequently encountered in the field (see ref. 1, p. 74). Those most usually applied to solid decompositions are summarized in Table 1. The demonstration that isothermal yield–time data for the decomposition of a particular solid satisfactorily obeys one of these rate relations is usually accepted as evidence that the reaction concerned proceeds by the nucleation and growth processes assumed in the derivation of that kinetic equation. Methods of testing such obediences are mentioned in Table 2, which also cites source references [1]. Conclusions from kinetic analysis are not always unambiguous and should be supported whenever possible by microscopic evidence concerning the geometry of interface development. Zero-order obedience (a constant reaction rate) in particular can be alternatively explained by several distinct and different reaction models (see ref. 1, pp. 84–86).

INTERFACE CHEMISTRY

The inaccessibility of the reaction zone, juxtaposed between the solid reactant and solid product, makes it difficult to elucidate the mechanism of the overall chemical change taking place within this thin layer (perhaps a few lattice units in thickness) of locally enhanced chemical reactivity. The total amounts of intermediates present may be very small and such participants may be expected to be unstable. These are, therefore, difficult to identify and to measure analytically, particularly in the presence of the much larger quantities of reactant and product, to which they may be expected to be closely related chemically. When a solid metal is present (perhaps a product) the magnetic and optical properties of the mixture are modified in such a way as to reduce the possibility of successfully using resonance or optical techniques. The identification of chemisorbed intermediates in catalytic-type interface reactions poses special problems. The mechanical separation of

reactants and products along the common contact is similarly unlikely to be achieved easily, since such treatment would be expected to destroy any fragile structures present. It must also be regarded as difficult to demonstrate the existence and, indeed, the relevance to reaction, of inter-lattice strain at the reactant-product interface.

Probably as a consequence of the paucity of direct experimental evidence relating to interface chemistry and the factors controlling reactivity, many interpretations of kinetic behaviour have identified the magnitude of the calculated activation energy with the energy barrier to reaction. This identification follows parallels with homogeneous reactions, since decompositions of solids obey the Arrhenius equation. Most kinetic studies report an activation energy and many report reaction frequency factors [3]. Information about the course of reaction can also be obtained from topochemical investigations [7].

In the particular kinetic studies individually discussed below, we wish to suggest that evidence concerning the mechanisms of reactions of solids can be obtained from detailed microscopic examinations of the interfacial zones, when considered with suitable support from other relevant observations. Accordingly, we propose a classification scheme of interface functions, intended to identify the reasons for the preferential occurrence of reactions at the reactant-product interfaces. The interpretations given assume, in some systems, a greater mobility of the species involved, extending to the participation of a liquid, than has been customary in the field. Such an involvement of dissolved or molten reactant explains the role of the interface in reducing the constraints on the decomposing entity, since the restraints imposed by the cohesive forces of the crystal are thereby withdrawn.

Three classes of nucleus are distinguished in our treatment. These are classified and described in the following paragraphs, and there may, of course, be others. Recognition of these structures requires high magnification microscopy, as is indicated by the examples in a subsequent Section.

(1) Fluid-flux nuclei

Nuclei of this type are envisaged as structures specifically developed to retain temporarily a proportion of a volatile product at the interface condensed as a liquid within which chemical reactions and/or recrystallizations occur. This model contrasts with the more usual view that the solid product offers no impedance to volatile-product escape, a conclusion based on the belief [1] that increasing amounts of residue do not oppose reaction, since interfaces advance at a constant rate. This kinetic behaviour is, however, also consistent with the fluid-flux representation if it is assumed that the liquid is confined to a thin zone of constant thickness at the interface, and beyond this the diffusive escape of gas is rapid through the wider channels permeating the bulk of the product nucleus.

(2) *Fusion nuclei*

Product melting, accompanied by eutectic formation on dissolution of the reactant in the expanding fluid formed, is also capable of explaining the sigmoid-shaped α -time curves. Localized onset of melting within which reaction proceeds will be referred to as fusion nuclei.

(3) *Functional nuclei*

Reaction occurs at the reactant-product interface induced by strain and/or heterogeneous catalytic breakdown of a chemisorbed intermediate at the contact. The product functions directly in promoting the chemical change. This is the most widely accepted explanation of interfacial chemical change.

NON-ISOTHERMAL KINETIC STUDIES

Kinetic measurements for solid decompositions under conditions of controlled (usually linear) temperature increase offer, in principle, the possibility that data from a single experiment can be interpreted to measure both the kinetic obedience [$f(\alpha) = kt$] and the Arrhenius parameters (activation energy, E , and frequency factor, A). A number of rising-temperature studies have yielded conclusions which agree satisfactorily with those found from comparable isothermal investigations, but more often inconsistencies appear. Since such doubts exist, non-isothermal measurements are sometimes supplemented by parallel constant-temperature work, a duplication of effort that offsets the advantages apparent in the former approach.

The central problem inherent in the kinetic analysis of non-isothermal rate measurements is the necessity to combine the three functions [$f(\alpha) = kt$ (the unknown isothermal rate equation), $k = A \exp(-E/RT)$ and the linear rate of temperature increase] in a form suitable for determining the fit to (α, t, T) measurements. Several approximate solutions to this problem, together with diverse variations, have been proposed and discussed in the literature [1]. None of these, however, has yet emerged as a preferred method, recommended for general use. A simplification of the analysis can result from the separate isothermal determination of the rate expression [$f(\alpha) = kt$] obeyed, followed by incorporation of this relationship into the subsequent calculation of A and E based on rising-temperature data [8].

Several reviews have been given of the expressions available for use in this field [1]. These cannot be adequately discussed here, though an indication of the less than satisfactory situation existing in the field is evident in the recent literature content analysis [3]. Of the 68 articles concerned with non-isothermal kinetic analyses in the literature sample, 9 also reported comparable

isothermal studies and only 3 of these showed satisfactory agreement between E values measured by both methods. The disagreements in the remaining 6 studies emphasize the difficulties inherent in the quantitative interpretation of measurements.

In this group of 68 papers a total of 29 evidently different methods were used for the calculation of E (and sometimes A). Authors seldom justified their choice of a particular method for their (approximate) calculations, though some approaches were used more frequently than others. Agreement of E values calculated by alternative methods for the same non-isothermal reaction was satisfactory in only 8 out of the 20 papers that reported duplicate, or several, parallel interpretations. It is clear from these conclusions, and from the discussions in the papers concerned, that general agreement has not yet been reached as to which of the numerous approximate methods of kinetic analysis available are reliable. The reservations expressed above are intended to emphasize the necessity for caution in accepting kinetic conclusions [$f(\alpha) = kt$, E and A] based solely on rising-temperature rate measurements. This is not intended as an adverse comment on the undoubted value of this approach to the determination of reaction temperatures, the elucidation of a sequence of chemical changes, the measurement of an enthalpy of reaction, etc. It is worth pointing out, however, that microscopic examinations often offer a more rapid and more reliable method of obtaining information about reaction geometry than non-isothermal studies. In the literature analysis referred to above [3], microscopy was employed in only two of the non-isothermal kinetic studies. This is most surprising, because rising-temperature interpretations are inherently less reliable than conclusions based upon constant-temperature studies, where microscopy was more frequently, but by no means invariably, used to confirm geometric conclusions.

MECHANISMS OF SPECIFIC REACTIONS

This section presents a number of brief mechanistic discussions of representative reactions selected to illustrate the principles of interpretation given above. Full accounts of these reactions are given in the references cited.

Dehydration of alums. (Fluid-flux nuclei)

Many of the earliest studies concerned with the theory of nucleation and growth reactions in solids selected alums as reactants. Since the mechanisms of chemical changes occurring at the reactant/product interface had not been investigated by high magnification microscopy, we extended work in this direction [9].

Kinetic and microscopic studies showed that after exposure to dehydra-

tion conditions (evacuation) the cleaved surface of a $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystal was significantly modified texturally by subsequent exposure to water vapour. The behaviour of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was different: on a first evacuation a small number of nuclei were formed but, after exposure to water vapour, followed by a second evacuation, a very much larger number of growth nuclei were produced. This was positive evidence that evacuation resulted in much more extensive modification of the alum surface than nucleation at a limited number of sites. The observations for $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ suggested that interface development may require water retention

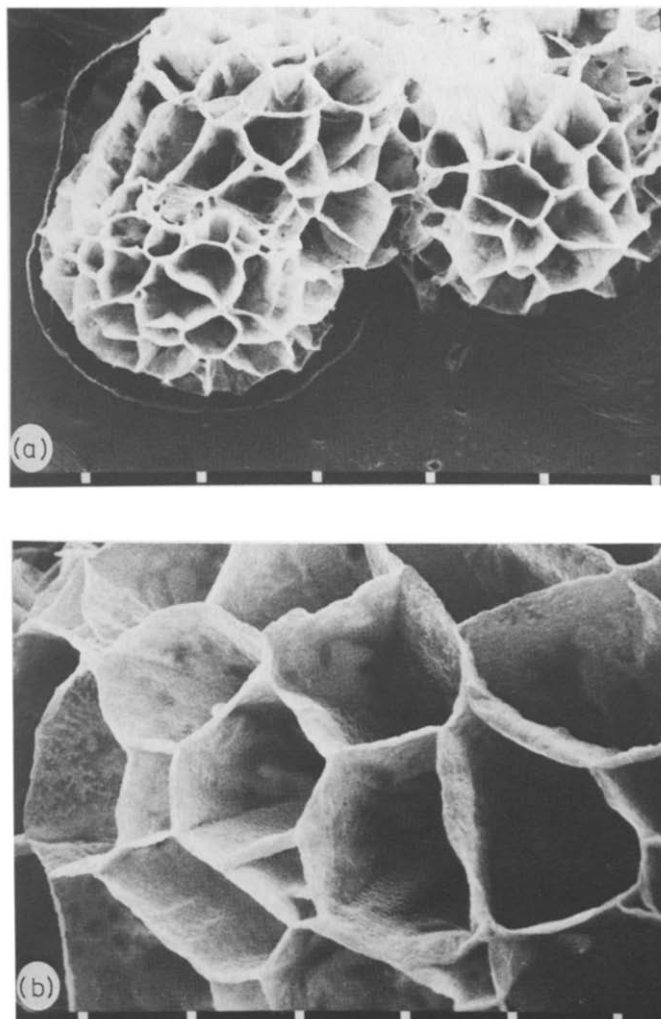


Fig. 1. Internal structures of fluid-flux nuclei formed during dehydration of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and revealed by replication followed by examination in the scanning electron microscope [9,10]. Interval between scale points at lower edge of photographs is 100 and 30 μm , respectively.

and this was consistent with the estimated pressures of water retained within the crack systems of nuclei, as revealed by replication techniques. We suggest that such retention of water at the interface promotes product recrystallization and accounts for the chemical activity within this zone. Typical crack structures of nuclei in $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, revealed by replication, are shown in Fig. 1 [10].

KBr + Cl₂ → KCl + BrCl. (Fluid-flux nuclei)

Although this is not a decomposition reaction, it is included here since it proceeds by a nucleation and growth mechanism at low temperature (< 350 K). Kinetic behaviour tended to be irreproducible and the power law was obeyed initially with a high exponent ($n \approx 6-11$). A previous investigation had suggested that interfacial strain induced imperfection proliferation in the path of the advancing interface, the structures of the square-section nuclei were complicated and had been incompletely established. This reaction appeared, therefore, suitable for study by microscopic methods [11]. Scanning electron microscopic examinations revealed that the reactant surface exposed within growth nuclei by cleavage after partial reaction (Fig. 2) was textured in a manner similar to that developed after exposure of a reactant KBr surface to bromine. Moreover, the planar facets of the intranuclear KCl product crystallites were oriented in (111) crystallographic directions (relative to KBr reactant), whereas the mean planar faces of the nuclei advanced normally to the principal axes of the crystal, (100), etc. This intranuclear texture, and the orange colouration of the growth nuclei, suggested the retention of liquid halogen at the advancing interface as the medium within which the chemical changes occurred. Such product retention was confirmed by iodometric titration ($\text{KI}/\text{Na}_2\text{S}_2\text{O}_3$) and explains the ability of SnCl_4 to accelerate the onset of nucleation. It is concluded that the liquid solvent medium permits the reaction to proceed through ionic intermediates [11]: dissolution $\text{KBr} + \text{Cl}_2 \rightarrow \text{K}^+[\text{BrCl}_2]^- \rightarrow \text{BrCl} + \text{KCl}$ precipitation.

Decomposition of ammonium dichromate. (Fusion nuclei)

Examination of lightly crushed samples of ammonium dichromate in the scanning electron microscope revealed the development of a froth-like residual material which contained numerous round, bubble-like holes. Figure 3 shows the internal texture of a reacted zone and also the spherical particles associated with onset of reaction on a crystal surface. Superficial bubbles were also formed, some of which were broken, permitting direct observational confirmation that the walls were thin.

These structures are believed [12] to result from the evolution of gas in a viscous liquid, the rounded surfaces indicating control by surface tension

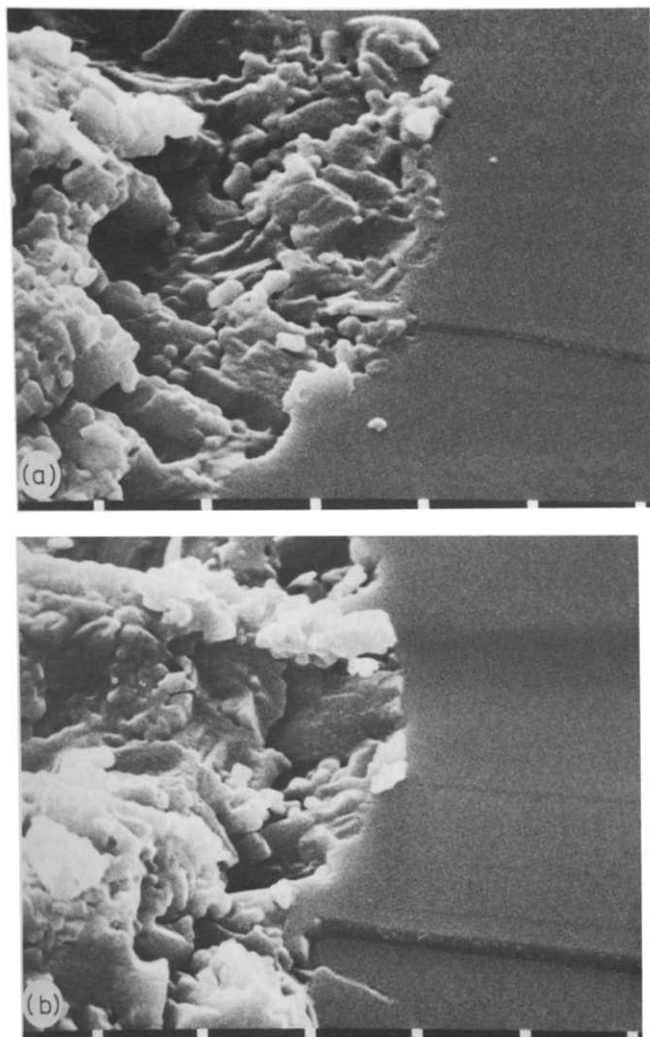


Fig. 2. Sections of reaction interface revealed by cleavage across nuclei [11] developed in the $\text{KBr} + \text{Cl}_2 \rightarrow \text{KCl} + \text{BrCl}$ reaction and examination in the scanning electron microscope. The rounded texture of surfaces and absence of cracking is consistent with retention of liquid halogen during reaction in these fluid-flux nuclei. Scale spacings both $3 \mu\text{m}$.

rather than crystallographic forces. Identical structures and textures were developed during the reaction of ammonia gas with chromic oxide (CrO_3) above the melting point of this oxide. From these microscopic observations and other evidence [12], we conclude that reaction occurs in the liquid phase, which may be temporary and locally restricted. The initial progressive increase in the amount of liquid present explains the predominantly sigmoid shape of the α -time curve.

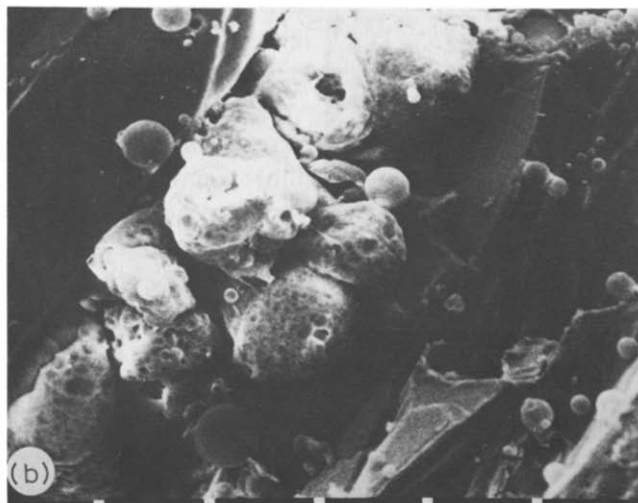
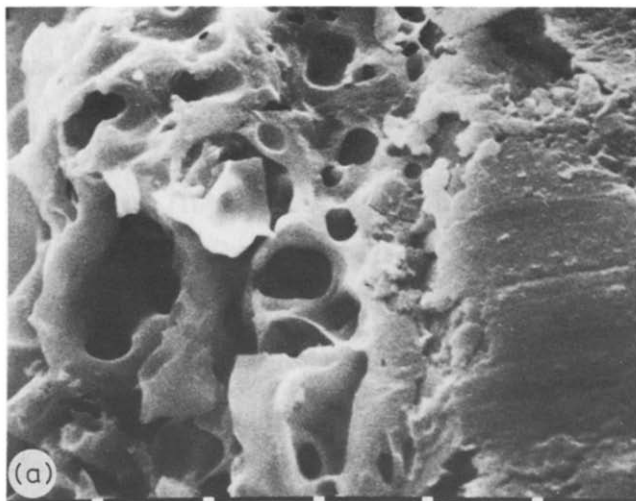


Fig. 3. Examination of partially decomposed and lightly crushed ammonium dichromate [12] showed the presence of rounded, bubble-type structures at fracture surfaces and spherical, froth-like zones, attributable to melting accompanied by volatile product evolution. Scale spacings 3 and 30 μm , respectively.

Decomposition of copper(II) malonate. (Fusion nuclei)

The kinetic characteristics of copper(II) malonate decomposition were unusual in being initially acceleratory (obeying the exponential equation) and subsequently undergoing a marked diminution (\times ca. 0.15) in rate at $\alpha \approx 0.5$ [13]. The first stage in this reaction is ascribed to the initial accumulation of liquid in which decomposition occurs, since the froth-like texture of the partially reacted salt (Fig. 4) is similar to that found microscopically in the decomposition of ammonium dichromate (above).

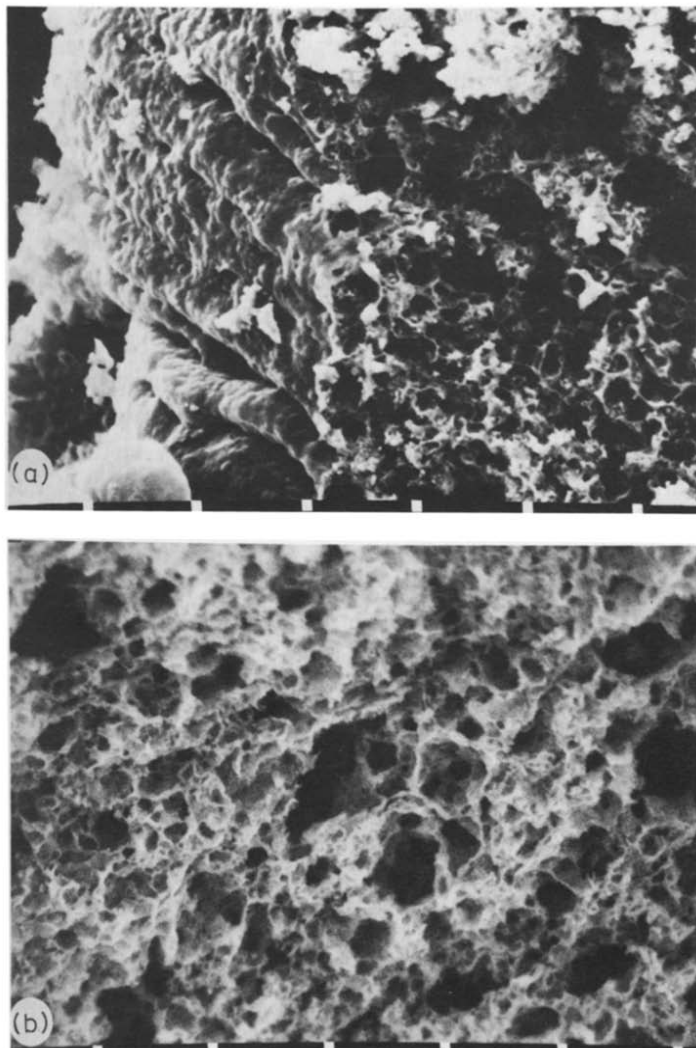


Fig. 4. Internal structures observed in partially decomposed copper(II) malonate [13], using the scanning electron microscope and a sample lightly crushed after reaction. Structures are generally similar to those in Fig. 3; there is evidence of a froth-like texture attributable to gas evolution in a viscous melt and reaction is not subject to crystallographic controls. Scale spacings both $10\ \mu\text{m}$.

Decompositions of metal carboxylates. (Functional nuclei)

Since metals catalyze the decompositions of carboxylic acids, a possible intermediate in the decompositions of those metal carboxylates yielding metal as product is the anion chemisorbed on the metal particles comprising the nuclei. This reaction mechanism has been discussed with reference to the decompositions of the following salts: copper formate [14], nickel formate [15] (and nickel squarate [16], though this is not a carboxylate), and silver malonate [17].

CONCLUSIONS

The purpose of this article has been to draw attention to particular features of the field of decomposition reactions of solids which, we believe, deserve critical consideration at the present stage of subject development. It appears to us that progress in the elucidation of interface chemistry has been slow but the evidence presented above may stimulate discussion as to feasible directions of future profitable advance. In particular, the classification scheme for nucleus function is intended to explore the possibility of more radical mechanistic representations of the zone in which chemical reactions occur. In contrast, we express our reservations concerning the value of the non-isothermal approach to quantitative kinetic measurements. Space precludes the detailed consideration that this topic deserves by virtue of its extensive and continually growing literature. It is a topic now well over-due for critical survey.

It is certain that the well-established and long-standing interest in the chemistry of solids shows no perceptible signs of abating.

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