

CHAPTER THREE

SOLID STATE REACTIVITY MODELS

3.0 Introduction

Any description of a reaction in the molecular solid state must implicitly take into account both a molecular transformation which is in the realm of chemistry and structural changes related to it which are normally considered to be more the province of physics. Various models which have been suggested to describe solid state reactions, with emphasis on inter and intra molecular processes are discussed below.

3.1 Topochemical principle and related concepts

The term ‘topochemistry’ was introduced by Kohlschuetter in 1919 when he produced colloidal Al_2O_3 inside the boundaries of an original $\text{KAl}(\text{SO}_4)_2$ crystal [1]. However, it was the work of Schmidt and Cohen [2] that formalized the topochemical principle and the related notion of reaction cavity, providing the first ‘model’ for the interpretation of chemical reactions in the solid state. In this model the concept of least motion was enunciated. The topochemical principle states that a ‘reaction in the solid state occurs with a minimum amount of atomic or molecular movement’ [2]. In the model the reaction is envisaged to occur in a fixed reaction cavity, where an especially suitable packing arrangement requires least molecular flexibility and atomic motion for transformation to take place. The model was particularly successful in establishing the products expected from a $(2\pi-2\pi)$ photo assisted reaction and a maximum bond separation of 4.2 Å between reacting centres was established.

Attempts to quantify this ‘hard sphere’ model, by Ohashi in particular, have permitted correlation of a quantified reaction cavity with reaction rates. In this approach the reaction cavity is defined ‘as the space limited by a concave surface of the spheres of the surrounding atoms around the reactive group in the crystal’, with appropriate radii chosen

for the measurement [3]. Remarkably, good correlation was established for the X-ray induced crystal-to-crystal reactions of a series of cobaloximes. Zimmerman and Zhu [4] have attempted to generate transition state molecules in the solid-state cavities and have proposed a ‘lock and key’ model for quantifying atom-atom interactions in the cavity.

The topochemical model has been most helpful in clarifying the course of a number of solid-state reactions and while further refinement of this approach has occurred, it is limited to those reactions that take place in the ordered crystal structure and without too great a disruption of this structure as the reaction proceeds. Consequently there have been reports of many reactions that do not fit the ‘model’ [5]. This arises since, the real solid has surfaces, grain boundaries, dislocations, substitutional impurities, occluded solvent and possibly other types of defects. Molecules at or close to these defects have a higher potential energy than those in the ordered regions and may be more reactive. Reactions at defects may sometimes merely lead to side reactions but they may also yield the only or the major product if the bulk of the crystal is unreactive [6]. Hence alternative proposals have been developed to rationalize reactivity in solid materials.

3.2 Local Stress

The importance of lattice stress in solid-state reactions has been suggested mainly by the research of Hollingsworth and McBride [7]. In this approach the reaction cavity is not regarded as a ‘passive cradle but as a press’. Thus, because of stress generated by a reaction, the intermediates often follow indirect trajectories rather than least-motion paths. The mechanical properties of the medium can therefore become as influential on reaction as the surrounding medium’s shape. This model predicts that enormous local stress fields will be produced in a cavity. It has been estimated that a 10% radial expansion of the cavity would require a cavity pressure of about 10 kbar, which is consistent with pressures that have been suggested for some reactions [8]. These findings indicate that the effect of local stresses must be significant in solid-state reactions. While the above concept is qualitatively useful, it is only recently that a general theory to quantify the process of chemical pressure has been proposed by Luty and Eckhardt [8]. In

this theory elastic multipoles (accounting for crystal elasticity) are introduced. The model permits for the quantification of both a reaction cavity and steric compression.

3.3 Structural phase changes

One manifestation of collective properties is a phase transition. Indeed, consideration of a solid-state reaction leads to the conclusion that, by its very nature, a reaction in a crystal must be accompanied by some change in the phase [8]. In this context, phase changes are understood to imply a change in the physical state of a material, excluding changes of a chemical nature. However, as noted by Dunitz [6], there is no clear-cut distinction between solid-state phase transformation and chemical reactions, only differences in the degree of cooperativity.

3.3.1 Thermodynamic aspects

Typically described by thermodynamics, phase changes are generally divided into two categories according to the Ehrenfest classification [9]:

- (i) First-order changes in which properties (such as energy, enthalpy, entropy, volume, *etc*) and crystal structure change discontinuously (*i.e.* first derivatives of Gibbs free energy with respect to temperature and pressure are discontinuous at the transition).
- (ii) Second-order (higher-order) changes in which the properties and the structure change in a continuous manner with no latent of heat of transformation (*i.e.* second derivatives of Gibbs free energy with respect to temperature and pressure are discontinuous at the transition).

The distinction between the two phenomena is often ambiguous. In general, besides melting, nucleation and growth of a new solid phase within an existing phase is first order, while transformations within the molecules that acquire orientational degrees of freedom, but with very limited translational motion (order-disorder transitions), are second order [10].

Provided the necessary state functions can be measured or calculated, the relative thermodynamic stability of a crystal phase may be evaluated according to its Gibbs free energy, given by $G = PE + E_{\text{vib}} - TS$, where PE is the packing energy and E_{vib} the vibrational energy. Thus the relative stability of a phase is determined by a trade-off between the combined energy ($PE + E_{\text{vib}}$) and the entropy term TS [6].

3.3.2 Structural aspects

The influence of structure on solid state reactions is well known [11]. From thermodynamic consideration alone, one cannot make any detailed statements about the actual structures or mechanisms associated with a phase change accompanying a solid state reaction. One of the early attempts of discussing phase transitions in structural rather than in thermodynamic terms was made by Bueger in 1951. He classified the various types of transformation in terms of changes in the bonding network according to structural criteria [6]. Although Bueger's discussion was directed mainly at inorganic mineral structures, one of the concepts that can be carried over to the domain of molecular crystals is the distinction he made between 'displacive' and 'reconstructive' transformations.

- Displacive transformation involves a distortion of one network into another, *i.e.* the initial structure can be imagined to deform continuously into the final one without any disruption. Since no energy barrier opposes a net distortion of this kind, transformation proceeds very rapidly with a speed equivalent to the transmission of heat through the structure.
- Reconstructive transformation involves the disruption of the old structure (network) and its subsequent reassembly into a new pattern, a process that would be associated with a very high energy barrier.

While actual phase transformations are more complex than the simplified processes put forward by Bueger, the emphasis on the structural change represented a shift from pure thermodynamics.

More recently, the principle of phase rebuilding has been extended by Kaupp [5, 12, 13] to describe structural phase transformations in molecular crystals involving chemical reactions. AFM studies have revealed that chemical reactions require long range-anisotropic molecular movements over several nanometers or up to hundreds of nanometers, with the movements being well directed vertically and/or laterally. The reactions work themselves from the surface down into the crystal with the reaction movement determined by crystallographic faces (guided by the initial crystal lattice) with reconstruction occurring over thousands of Angstroms. Eight characteristically different types of surface structures can be generated in the process and these have been classified according to their shape and kinetics of formation. If no molecular movement is possible due to particular features of the crystal packing, no chemical reaction occurs-even if distances between potentially reactive centres are very short ($<4.2 \text{ \AA}$) and their orientations appear favourable (as required by the topochemical principle). Numerous positive exceptions to topochemistry (solid-state reactions with large separations of up to 10 \AA) are now understood on the basis of the above description of molecular movement.

An important feature of the phase rebuilding model, which treats the whole crystal as a unit, is ‘the need of the new molecules for immediate accommodation with the crystal lattice, after their formation in solid-state chemical reactions’ [13]. As the product molecules have shapes that differ from those of the starting molecules, strain is created which has to be released by movements along the easiest ways the crystal packing allows (face dependency). Only if the chemical reaction has become so complete that the distorted original lattice cannot be retained, for thermodynamic reasons, does phase transformation occur in which mixed crystals of the starting material (with low amounts of product) transform into mixed crystals of the product with low amounts of starting material). Thus, it is frequently observed that initially formed surface features disappear on prolonged reaction at the expense of new features which tend to be considerably larger; in other cases the crystal ruptures upon phase transformation. Where crystal data have been available, it has been possible in all examples studied by Kaupp to correlate the geometric type of surface feature (due to phase rebuilding) with the molecular packing. Kaupp has thus concluded that ‘anisotropic molecular movements are the

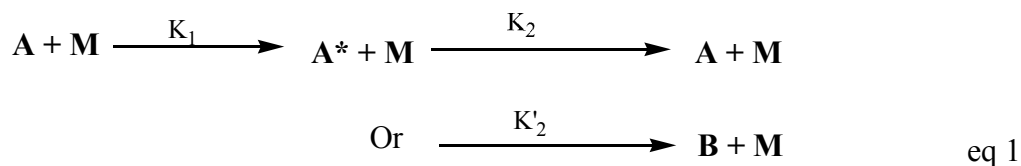
decisive criterion for solid-state reactivity, given the thermodynamic feasibility, of course' [13].

3.4 Solid State reaction kinetics

3.4.1 Thermal intramolecular reaction kinetics

A thermal reaction is one where the macroscopic state of the reacting system is described by temperature. Two alternative methods have been used in kinetic investigations of thermal solid-state reactions: in one, the temperature is held constant and the evolution of the system with time is followed (isothermal kinetic experiment) while, in the second, measurement of some characteristic of the solid versus temperature is made while, the temperature is varied with time (non isothermal kinetic experiment) [14]. Primary experimental data from these approaches are then manipulated to calculate kinetic parameters, such as reaction rate constants and activation energies.

Intramolecular solid-state reactions, such as intramolecular linkage isomerisation, racemisation, conformational isomerisation and importantly with regard to this work, *cis-trans* isomerisation, are diffusionless reactions in which no new chemical species need be transported to or from reaction sites for their occurrence. This is in contrast to for example, radical reactions in solids where diffusion of the reactive species in the sample plays an important role. Consequently, the above intramolecular reactions are viewed as unimolecular processes, making it appropriate to briefly review Lindemann's simple collisional mechanism for thermal reactions [15], which is given as:



where reactant molecule A undergoes collision with a surrounding heat bath molecule M to produce a reactive state molecule A* which either deactivates to reform A or reacts to produce product molecule B. The identity of M is immaterial; it could be A itself or the product formed in the reaction. The above mechanism is therefore a one-step collisional mechanism, but with a time lag introduced between the instant a molecule has received sufficient energy to react and the instant it actually reacts. Lindemann's scheme may be solved exactly to yield:

$$[A] = C_1 \exp(-kt) + C_2 \exp(-k't) \quad \text{eq 2}$$

Where brackets indicate concentration, C_1 and C_2 , and k , and k' are constants to be determined.

Although Lindemann's mechanism is formulated for solution and gas phase reactions, it can also be used in the description of unimolecular reactions in molecular crystals to the extent that it implicitly highlights the dual role the lattice plays – namely as solvent at an initial stage of reaction as well as becoming reactant itself in the course of the reaction. While M might denote a nearest neighbour to reactant molecule A in the molecular crystal (with association by means of nearest-neighbour interactions), this 'binary' process view tends to ignore the cooperative nature of the solid-state, where perturbation due to chemical transformation at a site is transmitted to other lattice vibrations, with activation achieved by phonon assistance [16].

Equation 2 above draws attention to an important aspect of solid-state kinetics. While concentrations of reactants or products are valid in homogeneous media due to generally uniform mixing, the same is not true for the solid state where reactions tend to be heterogeneous. Therefore, instead of concentrations, the degree of transformation (α) is used for kinetic analysis ($\alpha = \text{quantity reacted} / \text{original quantity in the sample}$); usually α is normalised to 1 with $\alpha = 0$ for unreacted material and $\alpha = 1$ for complete conversion [14].

3.4.2 Nucleation

The initial onset of a heterogeneous reaction in the solid-state is referred to as nucleation, which for the formation of a single nucleus involves conversion of a small volume of reactant into a stable particle of product. Once nucleation has occurred, the reaction takes place preferentially at the boundary between reactant and product phases as the nuclei grow, a process referred to as the growth stage of the reaction [17, 18].

Nucleation often begins at a surface, where the product is not totally surrounded by reactant molecules. It may, however, occur at special sites either on the surface or in the bulk of the solid. Such sites include linear imperfections (*e.g.* dislocations) and various types of point defects (*e.g.* Schottky defects, Frenkel defects, chemical impurities, *etc.*). Indeed, the surface itself may be regarded as a planar imperfection due to the inherent disruption of translational symmetry [19]. Consequently, the rates of solid-state reactions can depend on the history of the solid since the method of compound preparation and handling influences both surface area and the number and type of defects [17].

The more common laws of nucleation describing the number of nuclei N formed after time t are given below [18]. The number of potential nuclei forming sites is N_0 and k is the rate constant for the nucleation process, thus

(a) Instantaneous nucleation: $N = N_0$ eq 3

(b) Single-step, random nucleation among N_0 pre-existing sites; exhibiting exponential law behaviour:

$$N = N_0[1 - \exp(-kt)] \quad \text{eq 4}$$

or for slow nucleation ($kt \ll 1$), exhibiting linear law behaviour:

$$N = N_0kt \quad \text{eq 5}$$

(b) Multiple-step nucleation involving n steps for which $k_n t \ll 1$, results in power law behaviour:

$$N = N_0 K_0 K_1 \dots K_n t^n \quad \text{eq 6}$$

3.4.3 Growth

Following the development of stable product nuclei (termed the induction period), a generalized α -time curve (isothermal analysis) indicates an acceleratory period of growth of such nuclei, that can be accompanied by further nucleation, that extends to the maximum rate of reaction. Thereafter, due to impingement and consumption of reactant, the continued expansion of nuclei is no longer possible. This leads to the deceleratory or decay period, which continues until completion of the reaction [18]. It should be noted that one or more of these features may be absent or negligible; variations in their relative importance results in the appearance of a wide variety of different types of kinetic behaviour, that has been extensively reviewed in the literature [14, 17, 18, 20]

For solid-state kinetic models based on the formation and growth of product nuclei, it is of importance to know the topography of the process *i.e* the spatial development of the reaction and the propagation of the reaction interface. This is because different models of spatial propagation give rise to different shapes of kinetic curves (and hence equations). The classic, topokinetic Johnson-Mehl-Avrami-Kolmogorov-Yerofeev equation:

$$\ln(1-\alpha) = -kt^r \quad \text{eq 7}$$

thus describes first order behaviour (random nucleation) when $r = 1$, nucleation and growth (two dimensions) when $r = 2$, and nucleation and growth (three dimensions) when $r = 3$ [17].

It has been shown however, that the assumption of formal topokinetics (*e.g.* isotropic growth of nuclei) is not obvious, and often does not hold for real processes (nuclei can grow at *different rates* in different directions through the solid). When this occurs, the ‘feedback’ phenomenon is usually operative in which the state of the solid changes as the reaction proceeds; these changes affect further reactions, and so the feedback (either positive or negative) arises. Intermolecular reactions along with cooperative relaxations of mechanical stress (leading to structural distortion and local or general reconstruction) are often responsible for feedback [14]. In the vast majority of studies unimolecular processes in solids have been modeled according to first-order behaviour, by analogy with solution studies. This has often been unsatisfactory since even for the simplest unimolecular reactions, deviations from first-order laws can occur for a number of reasons which have been outlined in the literature [14]. In any event, because rate constants and activation parameters depend to a large extent on the model selected (recent papers have also commented extensively on the applicability of the Arrhenius equation to solid-state work and on the issue of variable activation energies for condensed phase reactions [21, 22, 23]), solid-state kinetic data should be accompanied as much as possible by supporting observations involving techniques such as optical and electron microscopy, and X-ray diffraction.

3.5 Monitoring Solid State Reactions

Various experimental techniques give information on the intermolecular interactions in solids. It has become more common to study the interactions in solids prior to the solid state reaction [24]. Solid state reactions are normally easy to carry out. However, the main disadvantage of solid state studies is often the characterisation of the reaction product, which is usually in the form of a polycrystalline powder whose characterisation requires solid state techniques [25]. It is more difficult to study the evolution or manifestation of the intermolecular interactions in a solid in the course of a solid state reaction (a chemical reaction, a phase transition, or a continuous structural distortion with no changes in chemical composition or molecular structure) and hence the kinetics of these reactions (though important) are poorly understood [26]. Below is a summary of

solid state techniques which are commonly used in monitoring solid state reactions most of which were used in the thesis.

3.5.1 Thermal Analysis

DSC: measures the amount of energy (heat) absorbed or released by a sample as it is heated, cooled, or held at a constant temperature. [27] Typical applications include the determination of melting point temperature and the heat of melting; measurement of the glass transition temperature; curing and crystallization studies; and identification of phase transformations. Melting is indicated by an endotherm and phase transformation is indicated by an endotherm in a DSC profile.

TGA: measures the change in mass as a function of temperature. The TGA profile can be used to analyze desorption and decomposition behavior, characterize oxidation behavior, set burnout or conditioning parameters (temperature/ramp rate/time), and determine chemical composition.

3.5.2 Spectroscopic Methods

(i) Transmission

IR: An infrared spectrum is characteristic of a particular compound providing information about its functional groups, molecular geometry and inter-/intra-molecular interactions

(ii) Reflectance

DRIFTS: This is a technique used to study reactions in the solid or powder form. The principles are the same as those used in solution IR spectroscopy *i.e.* to measure reflected infrared light. The technique is quite good for monitoring reactions of CO containing species as they have strong absorptions between 2400 and 1400 cm^{-1} .

The frequencies at which absorption occurs may indicate the type of functional groups present in the substance. Analysis of the fine structure of vibrational bands enables the study of interactions between different complex ions in the structure, and also reveals the perturbing effect of the environment on the molecule at a particular site in the crystal [27, 28].

Solid State NMR Spectroscopy: is helpful for studying conformations of molecules, their local environments in the solid, motions of molecules and molecular fragments. The chemical environment of specific nuclei is deduced from information obtained about the nuclei.

3.5.3 X-ray Diffraction Methods

The X-ray diffraction technique is an important tool for studying various intermolecular interactions [24]. It gives direct information on the distribution of electron density and on the atomic coordinates in the crystals. This can prove the existence of intermolecular interactions directly and provide information on geometric parameters of intermolecular bonds. Statistical analysis of data accumulated in the databases makes it possible to find interatomic distances, angles, structural patterns characteristic for particular types of molecular interactions.

Recent developments in X-ray diffraction have made it possible to study the evolution of intra- and intermolecular interactions in the solid state processes *in situ*. The structures of excited states of molecules and complex ions can now be obtained from diffraction experiments [29-32]. For single-crystal→single-crystal transformations the structural evolution can be studied by single-crystal X-ray diffraction experiments, so that both molecular structures of the products at the intermediate stages and the response of the parent structure to the reaction can be followed [24]. Manifestations of intermolecular interactions to the response of a crystal structure to a solid state chemical reaction can be followed by X-ray powder diffraction, if the reactant compound is not available as single crystals, or if the parent single crystals are destroyed as the reaction proceeds.

Variable temperature XRD is a powerful tool to probe reaction kinetics in solid state reactions since it permits simultaneous quantification of multiple solid phases. In order to distinguish between attractive specific interactions and simply short contacts with zero interaction energy in the structure, a crystallographic study of the inter atomic distances and angles in the structures at multiple temperatures should be completed by studying the temperature induced changes in the atomic displacement parameters, and also by measuring vibrational spectra [33]. The refinement of structures at several temperatures can provide information on the atomic motions and on the correlated atomic displacements in the crystal, and this information may be complimentary to the data obtained from NMR and IR spectroscopic methods.

3.5.4 Optical Microscopy

This technique can be used to study the intermolecular interactions in the crystal if the spatial propagation of a solid state process is followed. One can gain much information from the differences in the behaviour of different crystal faces, from formation of an interface in the course of the reaction and from the anisotropy of its propagation. The data can also be correlated with data obtained from other techniques to deduce the mechanism of a solid state process [24].

3.6 References

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