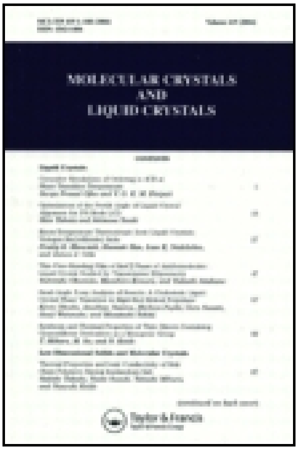

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Collective Interactions and Solid State Reactivity

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Collective Interactions and Solid State Reactivity

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The question of the quantitative energetics of organic reactions in solids is addressed by studies of the solid state reaction of 2,5-distyrylpyrazine (DSP). Crystal electronic spectra permit the role of excitons to be analyzed. Experiments are described which elucidate the evolution of lattice vibrational modes as a function of extent of the reaction and the relative motions of the molecules associated with those modes. A general theory of solid state reactivity is employed to interpret the structural and spectroscopic results to produce a coherent, comprehensive picture appropriate for solid state reactions

Keywords: topochemistry, mechanochemistry, solid state reactions

INTRODUCTION

What distinguishes crystals from other forms of matter? A phenomenologically based response could be that they exhibit extremely regular structure, often beautifully symmetric, and characteristic physical behaviors. Indeed, it is the symmetry that many would claim to be most distinguishing, but this is certainly not unique to crystals for molecules also display remarkably beautiful and intricate symmetry. It is a special kind of symmetry that renders crystals singular: *translational symmetry.* From this arises all aspects of crystal behavior that

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makes them so fascinating. Diffraction studies would be impossible without it. But structure is not the only property intimately affected by translational symmetry. In fact, all crystal physical properties, and as we shall see, many chemical ones, ultimately may be related to translational symmetry. Translational symmetry encompasses the many body (collective) attributes of the crystal in contrast to the single body properties emphasized by structure.

Investigations of molecular solids tend to largely rely on structural methods and crystal engineering principles are largely based on structural correlations. Often, these cleverly exploit the translational symmetry of the solid. However, studies that utilize the effect of translational symmetry on other properties of the crystal are rarely encountered. This is understandable since the conceptual and mathematical framework for these effects are less easily envisaged than are the corresponding structurally related aspects of crystals.

This is unfortunate because the non-structural properties arising from translational symmetry can also be exploited as have been the structural. Where this may have the greatest effect is in crystal engineering and the design of new materials. This is fundamentally a synthetic problem and it will probably be the synthetic chemist mastering the concepts of collective interactions of crystals who will be uncovering entirely new approaches to crystal engineering and devising novel materials.

Herein we discuss how crystal collective states, electronically excited and vibrational, significantly affect, or are themselves influenced by, chemical processes in molecular crystals. Another goal is to show how a crystal, a profoundly mechanical object, has its chemistry affected by perhaps the most common mechanical response of interest, *strain*, which itself can be related to the collective vibrational excitations of the crystal.

This agenda will be accomplished by examination of the photoreaction of the well-known 2,5-distyrylpyrazine (DSP) solid state photoreaction. The study will entail investigation of the electronic and vibrational energetics of the crystal. This will be augmented by placing the results in the context of a theoretical framework relevant to other research reported in these proceedings. First, the problem of the DSP crystal photoreaction will be presented. Then the electronic spectra and structure of the crystal will be discussed and used to explain the wavelength dependence of the photoreaction. Next, the role of lattice modes in the solid state mechanism of the photoreaction will be examined by investigation of the single crystal intermolecular vibrational spectra. These results will be interpreted in light of the phonon assistance model. Finally, all the findings will be discussed within the framework of a theoretical structure that emphasizes the mechanochemistry of solid state reactions.

THE DSP CRYSTAL-TO-CRYSTAL PHOTOREACTION

The [2+2] photoaddition of DSP in the crystal to form oligomers or polymers was reported by Hasegawa and co-workers.[1] In solution, DSP and its isoelectronic congener, P2VB, (Fig. 1) were observed to undergo polymerization by irradiation with a broad band of wavelengths in the UV-Vis. Both exhibited the same kinetic behavior and displayed no characteristics that significantly distinguished one from the other. Further, both crystallized in isomorphous orthorhombic structures.[2] But here the similarity ends. DSP displays a wave-length dependence of its photoreactivity not detected for P2VB. At wavelengths greater than 400 nm, the DSP monomer crystal reacts to give oligomers while at shorter wavelengths, high polymer is formed. The oligomer crystals can also be converted to high polymer by irradiation at shorter wavelengths. This wavelength dependence of the reaction products of DSP remained unexplained although a biexcitonic mechanism had been suggested.[3] The idea of involvement of excitons, collective excited electronic states of the crystal, is consistent with our investigation of collective interactions in DSP crystals.

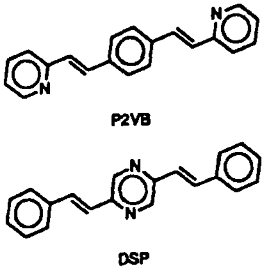

Figure 1

Another avenue requiring exploration in assessing the photochemical behavior of DSP is the role of phonon assistance.[4] This is a crystal reaction model where specific phonons, collective vibrational states of the crystal, have associated modal motions whereby reacting centers of molecules are brought in close proximity thereby enhancing the reactivity of the solid. The assisting phonons are soft modes whose frequencies approach zero during the course of the reaction. Such modes would have to be of very large amplitude (overdamped) and thus significantly anharmonic. Phonon assistance is viewed as the solid state analog of molecular collisions in fluid media reactions. Although not specifically relevant to the problem of wavelength dependence, the applicability of phonon assistance to the DSP photoreaction is of concern since it involves collective vibrational excitations of the crystal.

To investigate the role of collective excitations in the DSP crystal photoreaction, several approaches, experimental, theoretical and calculational, will be reported. The results of study of the DSP crystal's electronic structure by polarized specular reflection spectroscopy are examined together with results of exciton calculations.[5] Optical lattice modes investigated by polarized unmodulated[6] and piezomodulated[7] lattice mode region Raman spectra of the crystal are surveyed as a function of extent of reaction. Results of lattice dynamical calculations assist interpretation of the experimental findings. A general theoretical framework is utilized to elucidate the experimental results.

STRUCTURAL ASPECTS OF THE DSP PHOTOREACTION

By employing differences in the electron densities of reacted and unreacted DSP, Stezowski et al.[8] showed that little motion was involved in fromation of the oligomer and that the reaction is topotactic. The structural disposition of the monomer and oligomer molecules was found suggestive of a phonon-assisted reaction and lattice dynamical calculation indicated appropriate modal motions.

EXCITONS AND PHOTOREACTION WAVELENGTH DEPENDENCE[8]

Bright yellow DSP, initially obtained by synthesis, was purified by repeated and varied chromatography. The material was found to have approximately a dozen different contaminants, many highly colored. The pure material was nearly colorless. Reported long-wavelength photoreaction, probably due to sensitization by contaminants, was not observed in the pure material. To effect crystal-to-crystal reaction at all conversions, polarized light at 400 nm impigned on a face of the crystal where the transition moments of the electronic excita-tions had poor projections. This permitted homogenous irradiation through the bulk of the crystal and generated single crystals up to 100% conversion.

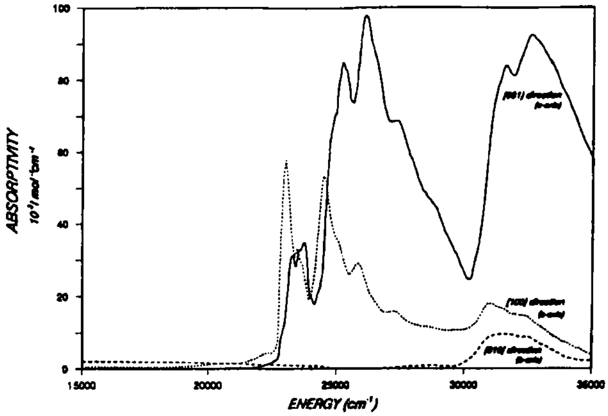

Figure 2

The DSP UV-Vis absorption spectra in solvents of varying dielectric constant cleary indicate the presence of $\pi^* \leftarrow$ n transitions near 400 nm with *no* absorption at wavelengths longer than 420 nm. Spectra for the *a*, *b* and *c* axes of the monomer crystal at 12K were obtained by transform of the corresponding polarized specular reflection spectra (Fig. 2).

The crystal spectra clearly differ from the simpler appearing solution spectrum and display more complex structure. This arises from the existence of collective electronic excitations of the crystal.[9] These form four exciton branches for each "parent" molecular transition. The weak $\pi^* \leftarrow n$ transitions are left essentially unchanged by the excitonic interaction. However, the lowest energy $\pi^* \leftarrow \pi$ transition forms four quite distinct branches one of which occurs in the same energy region as the 400 nm $\pi^* \leftarrow n$ transitions.

It is helpful to view the excitons dynamically. The $\pi^* \leftarrow n$ excitation does not migrate and remains localized; it is essentially a molecular transition. In contrast, the π-exciton moves rapidly through the crystal. In a static representation it would be called delocalized. However, the crystal was formed to be consistent with the electronic density of the molecule in the ground state. Thus, the lattice distorts locally to accommodate the different electronic distribution of the localized $\pi^* \leftarrow n$ excited state. The resulting defect creates a trap in the crystal into which π-excitons fall. This inhibits their migration and essentially limits their mean free path thus preventing excitation migration needed to generate the high polymer.

This mechanism is biexcitonic in the 400nm region since light in that region, and to lower energy, excites *both* $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ excitons. Shorter wavelength light excites only the π-excitons and no traps form. This permits the uninhibited growth of the high polymer. For P2VB, calculations indicate the $\pi^* \leftarrow n$ transitions occur to higher energy than the lowest π-exciton branch and thus oligomers will form by irradiation through a wavelength region above 400nm where the $\pi^* \leftarrow n$ transitions are found . Once this region is traversed, the P2VB will again generate high polymer.

Excitons' role in DSP photochemistry, and presumeably its congeners, suggests that chemists interested in exploring solid state reactions of organics have yet another interesting solid state phenomenon to exploit in devising and controlling new solid state reactions. The clear difference in behavior of the DSP crystal photochemistry from that seen in solution suggests novel and unusual solid state photoreactions remain to be found that are not based on structure but on the collective electronic states characteristic of crystals.

PHONONS AND SOLID STATE REACTIVITY[7, 8]

It is commonplace for chemists to follow the change of molecular vibrations in the course of a chemical reaction - particulary in a unimolecular one. Yet even though the reacting crystal may be regarded as a supramolecule undergoing a chemical transformation, little effort is made to observe changes in the crystal's vibrational spectra. Rather, observation is made of constituent molecular vibrations - a level once-removed from the actual process in the crystal. Lattice vibrations, phonons, may be especially informative of the nature of crystal forces that influence the solid state reaction.

The DSP crystal photoreaction is particularly suited for such a study since crystallinity is maintained through the course of the reaction. Use of polarized Raman scattering permits not only the observation of the optical modes of the lattice but also allows assignment of their symmetry. The latter is of importance for it relates to the nature of the modal motions, particularly those that may be involved in any phonon assistance.

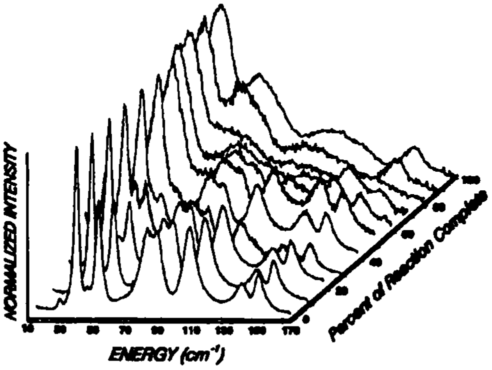

Figure 3

To assess the role of phonon assistance, more specific determination of the modal motion is required than assignment of symmetry. In addition, the anharmonicity of the phonon-assisting mode is of crucial importance. Piezo-modulated Raman scattering can be exploited to address these questions.[10]

Extent of Reaction and the Change of Intermolecular Vibrations[7]

The representations of the Raman-active rotational- vibrational modes of DSP are A_g B_{1g} B_{2g}, and B_{3g} of which each has three modes. Spectra were obtained from crystals ranging from 0-100% extent of reaction. Those for the B_{2g} modes are representative (Fig. 3). Great variance in intensity and frequency is observed as the reaction proceeds.

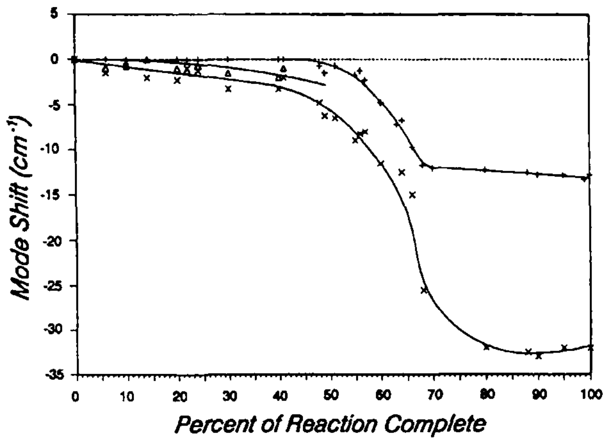

Figure 4

Fig. 4 presents a clearer picture of the evolution of these modes. One changes very little until better than 50% of the crystal has reacted. Another shows a decrease in frequency from the outset with rapid change occurring at about the same conversion as seen in the beforementioned mode. The third disappears at 50% conversion. This should not be surprising since the formation of oligomer will convert some external degrees of freedom to internal ones.

Anharmonicity and Modal Motions[8]

The role of excitons in the DSP photoreaction has been demonstrated but it remains to determine if phonon assistance plays a role. Participating modes must not only have motions that bring the reacting centers together but also must, by definition, be at the outset of the solid state reaction quite anharmonic due to their required soft mode behavior.

Piezomodulated Raman spectroscopy[11] (PRS) consists of application of a modulated uniaxial stress to a crystal and synchronous detection of the Raman scattering signal. The PRS response is proportional to modal anharmonicity. By variously orientating the direction of stress and observation of the phase of the PRS response, modal motions calculated from lattice dynamics can be tested. Thus, PRS is a direct way of assessing the role of phonon assistance.

The DSP photoreaction requires that the phonon modes assisting the reaction rotate reacting centers toward each other. Such modes will be Raman active. Lattice dynamical calculation in the harmonic approximation and treating the molecules as rigid bodies indicates that the 66.0 cm^{-1} A_g and 84.0 cm^{-1} B_{2g} modes have modal motions consistent with phonon assistance.

The PRS response of these two modes is unequivocal. The modal motions are consistent with those needed for phonon assistance and the lattice dynamical calculation. However, these modes are the least anharmonic of the modes of the same symmetry. Although they become quite anharmonic during the course of the reaction, this is a consequence of the reaction and the change of the lattice potential and is not indicative of phonon assistance. Thus, phonon assistance plays no role in the DSP photoreaction.

THEORY OF SOLID STATE REACTIONS: MECHANOCHEMISTRY[11]

How can we understand the rapid change of phonon frequencies when the reaction for DSP has reached 65% conversion? As the oligomers form, how do we factor the influence of the lattice into topochemical control? These and other questions have been dealt with using concepts such as the reaction cavity and steric compression. More quantitiative studies have considered local strain. But a quantitative, general structure is needed. In general, any isothermal process in the crystal involves a change in the free energy and is usually accompanied by a change of volume, *i.e.* $-(\partial F/\partial V)_T$. This is clearly a pressure and, since we are considering mainly chemical processes, it is called the chemical pressure.

Organic solids consist of well-defined but weakly interacting molecules. During the course of some crystal physico-chemical process, properties of the crystal change, *e.g.* molecular displacements or, equivalently, the internal strain. The changed properties are coupled to the local stress through a response function that is related to a single molecule susceptibility that is a function of parameter(s) describing the property of interest. This susceptibility may be related to anisotropic displacement parameters (ADPs). Thus, a local stress field would be coupled to molecular displacements by a response function that is, in the mesoscopic limit, a function of the elastic constant tensor. In this limit, the molecular displacements may be represented by strain which is related to acoustic phonons in the zero wavevector limit.

In a solid state reaction, local stress is created by the product molecule. As the reaction proceeds, the crystal is essentially a solid solution. The product molecule perturbs the reactant crystal and this costs energy at the site at which the product is formed. This can be represented by excess forces at the site, the assemblage of which may be regarded as the "applied" field leading to an induced structural change, the deformation. At a site there is an arrangement of excess forces that join the center-of-mass of the perturbing molecule to the atoms forming the reaction cavity. These forces form a distribution about the perturbing molecule which defines the reaction cavity. The negative of these forces defines the steric compression. The isotropic part of the local stress formed by these forces is the chemical pressure. Thus the reaction cavity and steric compression are joined. Indeed, the two can be incorporated into an elastic multipole description of the perturbing species.

The displacement vectors describing the deformation by the force distribution can be expanded in a series which formally is identical to that of the multipole expansion, *i.e.* dipole, quadrupole, octapole etc. terms. The equations describing the interactions of the multipoles with each other and with fields are formally the same as for more conventional multipoles. The elastic multipoles explicity embody the shape of the reaction cavity and the local forces' distribution. The distribution in the reaction cavity can be though of as "shaped" by the frontier orbitals participating in the reaction and the elastic multipole expansion as being determined by the angular distribution of those forces.

The interaction of the elastic multipoles decreases the energy of the crystal by the magnitude of the lattice deformation energy, the mechanical analog of the lattice polarization energy. The deformation energy is negative and stabilizing and arises from interactions of perturbations at different sites. The deformation potential can be decomposed into the self-energy of the perturbed cavities and their interactions with prodcuts. The self-energy is the energy required to place the individual product molecules into the elastic medium. The total deformation energy has the same role in a solid state reaction as the solvation energy does in a liquid state one.

After appropriate mathematical manipulation (renormalization) an Ising Hamiltonian can be formulated which embodies both a field (Δ) and coupling term (J). From this an activation energy, ΔE_{act}, can be calculated which is a function of the energy difference of monomer and product molecules as well as the deformation potential that depends upon the correlation function between perturbations. This can be expressed as a function of the average concentration of perturbations and thus makes the activation energy concentration dependent.

The J-term represents both direct and indirect interactions. Calculation of the free energy change shows that solid state reactions can be modeled by an interacting boson gas ($J \neq 0$) where the interaction between perturbations arises from local chemical pressure and is mediated by an elastic strain field. For a reaction $\Delta \neq 0$. The J-term determines whether the reaction occurs in an ideal ($J=0$) or non-ideal ($J \neq 0$) solid solution thus indicating that the strength of the interaction between perturbed sites dictates the homogeneity of the reaction.

The picture is thus one of product molecules embedded in an elastic medium, the lattice of the reactants. Local strain fields due to perturbations "stretch" the host lattice to its elastic limit. This is exceeded when the separate strain fields couple thereby leading to a new lattice potential, that of the product.

THE SOLID STATE MECHANISM OF THE DSP PHOTOREACTION

The above model provides a coherent explanation of the observations. Irradiation of the DSP crystal creates electronically excited molecules with energy ΔE^{0} leading to a $\pi^{*} \leftarrow n$ localized exciton. This occurs due to self-trapping which represents a feedback effect of the chemical pressure due to the excited molecule. The self-trapped state is of energy $\Delta = \Delta E^{0} - \Phi_{def}$ where the deformation energy must be larger than the exciton bandwidth so the localized state will be well-separated from the band. Φ_{def} is related to how strongly the change in van der Waals energy on excitation depends on the molecular displacements. Implicit is the assumption that energy gained by the crystal due to deformation is used to create self-trapped, excited molecules.

For DSP, ΔE_{act} can be found by approximating the potentials for two states as being parabolic (Fig. 5). Since the only structural change is due to internal strain, the intersection of the two potentials can be used to obtain $\Delta E_{act} = [\Delta E^{0}]^{2}/4\Phi_{def}$. This clearly shows that the activation energy will be significantly lowered by large changes in the dispersion energy between ground and excited states, *i.e.* by large values of Φ_{def}.

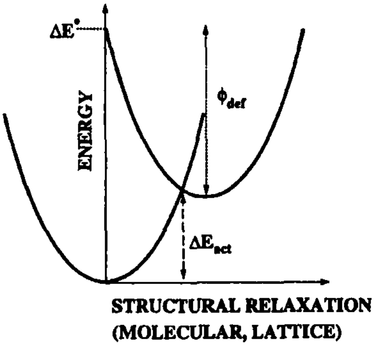

Figure 5

For DSP there are two separate excitons and thus two different ΔE^{0} terms with specfic relationships to their respective deformation energies. The closer these values are, the larger are the oligomers that can be formed. In this view, the 400 nm excitons differ significantly from the Φ_{def}'s but those excitons at higher energy are closer in magnitude and thus larger polymers are formed.

The oligomers create local stress fields that are accommodated by the monomer lattice. At approximately 65% conversion, the monomer lattice's elastic limit is exceeded, *i.e.* the elastic dipoles couple to effect a global change in the lattice potential to that of the product crystal. It should be noted that the actual physical distance between the dipoles is not necessarily a measure of the strength of the interaction. Indeed, regardless of the distance between the local stresses, when the lattice is transformed, coupling of the stress fields has occurred. This can happen at extremely low conversions, *i.e.* less than 1%, which is where the elastic limit is most valid.

CONCLUSIONS

Collective states, excited or vibrational, play a crucial role in the reactivity of crystals. Excitonic states are of particular importance in solid-state photochemistry. In these, as well as all other solid state reactions, the reaction pathway is largely dictated by the mechanical properties of the solid. Consideration of the elastic properties of the reactant lattice provides a general formulation of the mechanical role of the lattice in control of solid state reactivity. The DSP photoreaction demonstrates the importance of considering a solid state reaction from the viewpoint of collective interactions. In the design and study of solid state reactions, exploitation of collective excitations of the lattice may prove to be an interesting, important, and useful strategy.

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