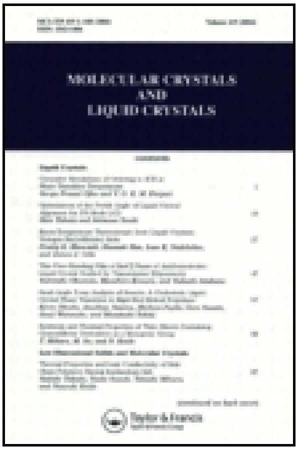

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Mechanochemistry: The Last Energetic Frontier

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Mechanochemistry: The Last Energetic Frontier

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A model for the direct introduction of mechanical energy into electronic degrees-of-freedom of molecules in crystals is discussed. This model is related to the hypothesis of HOMO-LUMO gap closure for detonation initiation. However, it is demonstrated that complete gap closure is not required for chemical processes to occur with the amount of closure related to chemical hardness. A new area of mechanochemistry can be developed where novel chemistry can be found. It is proposed that the term "mechanochemistry" be limited only to those chemical processes that are not driven by the thermalization of the mechanical energy.

Keywords: chemical hardness; deformation potential; detonation; DSP; mechanochemistry; solid-state reaction

INTRODUCTION

Why are solid-state reactions of interest? Specifically, why are those of organic crystals worthy of study? We are, in the main, surrounded by solid matter and yet the overwhelming amount of study of chemical processes deals with reactions in solutions. Chemistry in crystals differs significantly from these for solid-state reactions occur in a diffusionless environment. Because of the restrictions of geometry and the relative orientations of reactants, there is typically a unique reaction pathway leading to specific products. In the case of crystal-to-crystal reactions, a quantitative yield of a single product is usual. Such products may not correspond to the high yield products produced by the same reaction in a fluid phase, and may even be of low or no yield

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in such phases. The absence of solvents suggests that solid-state reactions may be more environmentally friendly than their solution counterparts. In addition, solids may lead to novel syntheses and thus the production of unique materials. For the same reasons organic chemistry itself is a major branch of chemistry, there is good reason to focus on organic solids.

Reactions invariably involve some kind of transformation of energy. This is of such importance that the classification of the chemistry may be according to the energy that is involved with the reaction. Heat, electricity, and light are forms of energy that are associated with chemical reactions. However, there is a major form of energy that is not commonly considered: mechanical energy. One reason mechanical energy has not been a major concern is the fluid phases in which most chemistry is performed do not lend themselves to interesting use of mechanical energy. An even more likely reason is the trivial fate of mechanical energy, first recognized by Count Rumford: it degrades easily to heat. Thus traditionally, to the chemist, mechanical energy is themalized and the normal chemistry based on heat is operant. This is exemplified by sonochemistry where mechanical (acoustic) waves are used to generate heat. However, the chemistries based upon the non-mechanical forms of energy are characterized by their *direct* conversion to drive chemical processes. The question arises: can mechanical energy also be so transformed and, if so, how? To be consistent with the chemistries based on other forms of energy, e.g., photochemistry, the term *mechanochemistry*, that now has various uses, should be restricted to this direct introduction of mechanical energy into a chemical system. The question is of particular relevance to solid-state chemistry since solids have, by their very nature, significant mechanical properties such as compressibility and hardness. In fact, there is ample evidence for mechanical forces affecting solid-state reactivity. The essential problem is to see how the direct introduction of mechanical chemistry into molecular degrees of freedom can be achieved and to postulate a model that describes the process.

There are mechanochemical processes that remain unexplained. In spite of nearly a millenium of use, the detonation of explosives is not understood. There are many examples of reactions between solids resulting from grinding. This is a current problem in pharmaceuticals where grinding, as well as tableting, lead to “browning”: the generation of impurities due to unforseen reactions during mechanical processing. There also remains controversy of how triboluminescence of some materials is not related to the emission of the ambient gas.

The goal of this paper is to discuss a proposed model for mechanochemistry [1] that is based upon a more general formulation of a theory of solid-state reactivity [2]. The next section will review current concepts used in organic solid-state chemistry to illustrate how mechanical processes are involved. The 2,5-distyrylpyrazine (DSP) crystal is used as an example system, exemplifying the role of mechanical forces in a prototypical crystal-to-crystal organic solid-state reaction. Next, current mechanochemical models are discussed with emphasis on one that not only accounts for known phenomena, but also has some predictive power. Another objective is to present a conceptual, and admittedly heuristic, framework of the model largely free of mathematical detail but, unfortunately, with the sacrifice of specificity and clarity that comes with a more quantitative treatment. The paper concludes with discussion of outcomes of this model.

CONCEPTS FOR ORGANIC SOLID STATE REACTIONS

The statement of the topochemical principle, that “a solid-state reaction will proceed along the path which requires the least amount of movement of the atoms or molecules involved” [3], together with the corollary that distances between reacting centers should be no greater than 420 pm, may be regarded as the fundamental phenomenological rule for solid-state reactivity. Clearly, the postulate carries mechanical implications. Further conceptual expansion was achieved with the suggestion of a reaction cavity: “a region of the crystal surrounding the reacting species and product” [4]. This could be considered as the introduction of a defect into the host (reactant) crystal lattice. Whether this view is chosen or not, the reaction cavity must certainly be associated with some kind of local mechanical deformation. Actual involvement of the lattice dynamics was suggested by the proposition of phonon-assisted reactions where “certain collective vibrations (phonons) of the crystal may coincide with motions along the reaction coordinate” [5]. This was complemented by the idea of steric compresssion, “a force acting at or near the reaction site that influences the atomic motions along the reaction coordinate” [6]. The crucial influence of local strain on solid-state reactions was demonstrated in a series of studies on the photodecomposition of peroxides [7]. All of this work clearly points toward the importance of the role of mechanical energy in influencing solid-state reactions.

These concepts, when coupled with experimental findings, are qualitative and essentially phenomenological. In order to formulate a more quantitative picture, the problem must be framed in terms of the energetics of the system. The fundamental physical question is: How do the potentials of reactant, product and lattice interact and modify each other during the course of a solid-state reaction when the system is stimulated by mechanical energy?

Thus mechanical properties are intimately involved with the chemical behavior of solid-state reactions. The elastic properties of the reactant crystal are particularly relevant to the intermolecular forces that hold the crystal together and that must be modified during the course of the reaction. It is important to note that these properties arise from collective interactions of the molecules and are not easily associated with a single molecule or even a small cluster of them. These attributes, all associated with the mechanical properties of the crystal, are necessarily implicated when mechanical energy is imparted to the crystal, i.e., the elastic response of a crystal to an external stress must be integral to any mechanochemical event. It is necessary to examine the role mechanical properties play and to identify the non-thermalized mechanism of transfer of mechanical energy from the crystal to the molecules. An important consideration is the assessment of the extent these properties are modified when the crystal is subjected to stress. For simplicity, they are usually assumed not to change significantly.

MECHANOCHEMICAL MODELS

The previous discussion has shown that mechanical properties are intimately involved with the course of a solid-state reaction. This does not indicate how mechanical energy, which must be mediated by the mechanical properties of the crystal, becomes available for direct molecular excitation.

It is useful to examine those solid-state reactions that are most responsive to mechanical excitation, explosions. When a crystal of an explosive is struck, a shockwave is injected into the solid resulting in detonation. If the mechanism for this process can be found, then it should be generally applicable to other mechanochemical events. The mechanism sought is for the *very initial event* for detonation. Once the process is begun by causing molecules to break bonds, then the tremendously complicated chemistry and intricate disposition of energy associated with the detonation wave takes hold. However, this does not involve the fundamental question of how mechanical energy is directly introduced into the molecular degrees of freedom.

It is useful to review the physics of the various kinds of chemistry, based on the nature of the source of energy. Figure 1 schematically depicts how thermo-, photo- and electro-chemistry are explained in terms of molecular energetics. In the case of heat, reactivity occurs by exciting the molecule's vibrational manifold. Sufficient heating will lead the molecule's vibrational energy to "climb" to the top of the

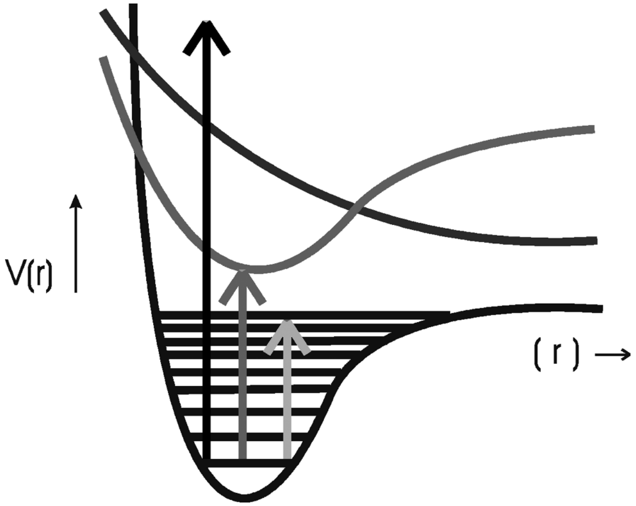

FIGURE 1 Potential energy diagrams showing thermal (short line), photo- (intermediate length line) and electrochemical processes. A mechanochemical process would drive the system up the repulsive part of the ground state potential.

vibrational ladder and thus dissociate. In photochemistry, a photon excites the molecule to an excited state, and it is that state that suffers chemical reaction. It is more difficult to depict electrochemical events with such a simple diagram but, crudely, it may be envisaged as a process involving the removal of an electron(s) into the HOMO (or other bonding orbital) or insertion of an electron into the LUMO.

But what happens when mechanical stress is applied? Of course, it must be applied to a ponderable body and not to an individual molecule. Nevertheless, the energy must enter the molecular degrees of freedom in some way. An appealing approach has been proposed whereby the energy of the shockwave is absorbed by the "phonon bath" of the crystal [8]. These excited lattice vibrations are pumped to high populations by the extreme compression of the shock wave. A molecule with sufficiently anharmonic, low-frequency, vibrational modes, termed "doorway modes," that are approximately twice the frequency of the phonon fundamentals, can then couple with the phonons. This would allow the energy to flow into the vibrational modes of the molecule. At this point, the process would then be the "ladder climbing" associated with thermochemical reactions. The model is, essentially, a thermalization of the mechanical energy. The model quite elegantly addresses the most common case of degradation of mechanical energy to heat.

However, it takes less than 100 femtoseconds for the shockwave to traverse a molecule, a time too short for slow thermalization processes. Only excitation of electrons is sufficiently fast to respond and to absorb the large amount of power associated with the shockwave. Gilman [9] pointed out that closure of a molecule's HOMO-LUMO gap could be induced by mechanical shear, a condition consistent with a shockwave. When this gap closes the electrons become delocalized leading to "metallization." The resulting "plasma" is unstable when the shockwave passes and thus leads to detonation.

It has been shown that some products of detonation are the same as those found from photodecomposition of the energetic material [10] and that the products, especially at the outset, are not undifferentiated. Thus, a model must be found that provides for this observation, a difficulty for a metallized system. Based on the concept of chemical pressure and a previously proposed model for solid-state reactivity, Luty, Ordon and Eckhardt [1] have formulated a model that is consistent with all observations.

Study of Figure 1 readily leads to understanding the basic concept that is a generalization of the HOMO-LUMO gap closing previously proposed. When suffering the extreme compression of a shockwave, the close-packed molecules of the crystal are forced against each other such that they undergo some kind of shear. This will involve compression. This forces movement up the repulsive part of the potential, a region of the potential rarely considered by chemists. Since this segment of the potential is bound, the energy of the molecule increases rapidly with compression until there is intersection with the potential energy surface of a higher energy state. At this point, the intersecting states must mix.

The first-order model considers only mixing of the HOMO and LUMO. This leads to a *distortion-induced molecular electronic degeneracy* (DIMED) that produces what may be regarded as a new ground state that is consistent with the molecule's response to the shockwave. The process involves both inter- and intra-molecular transfer of electrons. The resulting instability leads to chemical reaction. It should be emphasized that this will occur before metallization, i.e., before complete closure of the HOMO-LUMO gap. The point at which this occurs depends upon the specific material. Conceptually, the situation parallels that of kinetic theory for electron transfer reactions.

The Example of 2,5-distyrylpyrazine

The solid-state, crystal-to-crystal photoreaction of DSP, a readily polymerizable molecule in solution, is a well-studied system that exemplifies many of these concepts [11]. Further, it shows the role of strain and defects in the solid-state reaction. Initial studies showed that the DSP crystal's products were dependent upon the frequency of the exciting light. High polymer is obtained when light of frequencies greater that $25\,\mathrm{k}K$ ($1\ K\mathrm{ayser} = 1\,\mathrm{cm}^{-1}$) irradiates the sample whereas at lower frequencies only oligomers are obtained. This has been explained by an excitonic mechanism wherein highly localized $\pi^* \leftarrow n$ excitons [12], which are only created at frequencies below $25\,\mathrm{k}K$, lead to production of oligomers. At higher photon energies, delocalized $\pi^* \leftarrow \pi$ excitons, essentially excitation energy that can travel through the lattice, are able to continually "feed" energy for the growth to higher molecular weight polymers. The growth is only stopped when the $\pi^* \leftarrow \pi$ excitons fall into traps in the crystal such as defects. Thus, the solid-state reaction is driven by direct excitation of the reactant crystal by electromagnetic radiation.

Mechanical properties mediate the lattice, and it has been shown through following the frequencies and intensities of the Raman-active DSP lattice modes as a function of extent of reaction, that the elastic properties of the host (reactant) lattice determine when the transformation from the reactant to the product crystal occurs. In the case of DSP crystals, this transformation occurs at a fairly high conversion of 65%. The conversion is driven by the build-up of local strain fields around the product molecules. As the number of product molecules increases and the surrounding strain fields increase, a point is reached where the local strain fields couple and drive the transformation to the product lattice. This is the point where the elastic limit of the reactant lattice is exceeded, and it can no longer retain itself. Of course, in many solid-state reactions the strain can be so severe that it causes "destruction" of the crystal lattice. This picture complements the previous strain studies and demonstrates that both the reaction cavity and steric compression fit the model of the strain field and its development during the course of a reaction in a crystal. The salient point is that the elastic properties of the reactant lattice "control" the reaction pathway and it may be expected that, if possible, products will grow into the more compliant regions of the lattice. However, the product lattice may also be generated from large, cooperative motions of the reacting species.

Depending upon the elastic behavior of the surrounding lattice, these forces will vary according to the resistance that is met. This resistance and its magnitude, may be identified with steric compression. Both of these can be seen to be aspects of a more general quantity, the chemical pressure [13], that may be quantified. Thus, the elastic properties of the reactant lattice strongly influence the nature of the reaction in the solid. If the parent crystal is softer in one direction than another, this may be expected to influence the ease with which product is formed and the orientation it may adopt.

The local strain fields about product molecules will be isolated at small product concentrations, but as the amount of product builds, the strain fields are no longer isolated and they will couple. This coupling will drive the system to the daughter lattice. However, depending upon the potential energy surface of the latter, shattering of the crystal during the course of the reaction may be observed because of incommensurate lattice parameters. In fact, this is usually the most common fate of solid-state reactions.

This demonstrates the importance of the role of mechanical properties in a solid-state reaction. The energetics certainly arise from the mechanical properties of the crystal, but their role is quite different from the question of direct conversion of mechanical energy to chemical degrees of freedom. The mechanical interactions described by the DSP solid-state reaction do not involve the internal modes of vibration or electron distribution in the molecule. In fact, it is the photonic energy that drives the process by direct excitation of the molecules and not mechanical energy. The mechanical processes in the solid-state reaction are responsive to the generation of product and are not initiatory. Investigation of this requires a model that details the fate of the mechanical energy that is introduced into the lattice.

THE MECHANOCHEMICAL MODEL AND MOLECULAR HARDNESS

The application of mechanical energy is most often achieved by application of stress, usually compression, to the crystal. To involve the molecular degrees of freedom, Gilman has pointed out that it is necessary to have shear stress since hydrostatic stress is not expected to significantly affect the geometry of the molecule, save through decreasing its size. When driven up the *bound* repulsive part of the potential, an intersection with a higher energy state will eventually occur. When this happens, mixing of the ground state potential and that of the upper state will occur. Depending upon how steep the repulsive part of the potential is, there may be nearly simultaneous mixing between several states. However, consideration is restricted to the simple two-state situation, specifically mixing that involves HOMO-LUMO mixing.

This is an *electronic* process since only electronic states are capable of response on the timescale of the shockwave and are able to provide absorption of the large energies involved. Further deliberation leads to the conclusion that the governing condition is not the timescale of the mechanical event, but rather, the amount of mechanical power that must be accommodated. When the power is low, then thermalization is the expected process but when it is high, the vibrational modes cannot store the available energy efficiently and only the electronic modes would have that capacity. It is the latter that is of chemical interest.

Molecular hardness, η, measures a molecule's resistance to electronic change [14]. It is defined by:

$$\eta = \frac{1}{2}[I - A]$$

where I is the ionization potential and A the electron affinity. This is relevant because a change in the electronic distribution must be associated with the high mechanochemical power. Hardness' importance arises because it is tied to both the deformation of the molecule as well as to how the molecule packs in the crystal.

The specific mechanochemical reaction of detonation initiation has been used to guide thinking about mechanical energy into molecular degrees of freedom, but the mechanism need not be specific to this type of reaction. Whatever chemistry may arise, it will be associated with the deformation-induced state mixing that leads to the decrease of the HOMO-LUMO gap. It is expected that different higher energy electronic states will mix differently, since they will have different electronic distributions.

In the simple model under consideration, deformation leads to the closure of the HOMO-LUMO gap. As the gap decreases, the state mixing may be expected to increase. Alternatively, as the hardness decreases, the mixing will become greater. Thus, for the "metallization" model, $\eta = 0$. But is complete HOMO-LUMO gap closure necessary for a chemical reaction, or for detonation initiation in particular?

To address this, knowledge is required of how the change in energy on closure of the gap is related to the molecular hardness. The process can be envisaged as a sequence beginning with an initial distortion due to the stress that affects the electronic energy of the molecule and thus alters its hardness. The change of the hardness must lead to a change in the energy of the HOMO-LUMO gap that leads to state mixing and a new set of states. Complete closure is not required, but rather, a critical deformation must occur wherein the new potential surfaces develop. The resultant lower energy potential surface can be viewed as the compressional "ground state" (CGS) that is found at some critical value of the HOMO-LUMO gap closure.

In the case of detonation initiation, the higher energy state that is mixing is either dissociative or leads to dissociative character in the CGS. This is illustrated in Figure 2, where it is shown that some

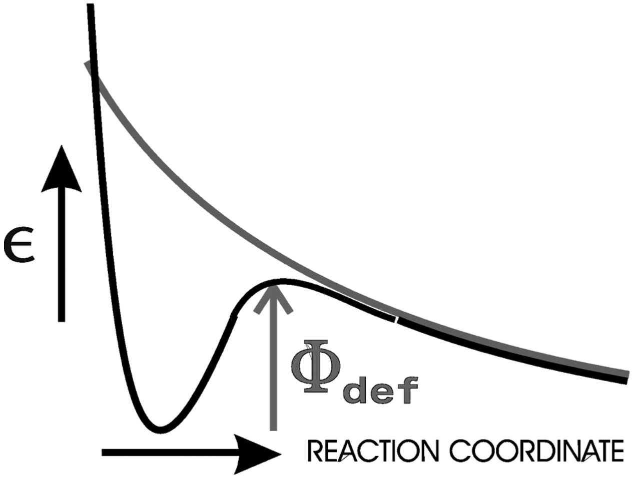

FIGURE 2 A "kinetic" plot showing the CBS (dark line) resulting from the mixture of the unstressed ground state and a dissociative excited state (light line). The role of the deformation potential in achieving detonation is shown.

critical deformation energy exists that allows the system to overcome the barrier between the bound portion of the potential and the dissociative tail. Once overcome, detonation initiation will ensue. However, if the CGS arises from mixing of two bound states, then the CGS itself should, because it differs from the two mixing states, produce new chemistry much akin to the photochemical products produced by photoexcited states. This holds promise for a new area of solid-state chemistry.

Another way of thinking about this phenomenon is to envisage the reverse process where photoexcitation to an excited state of a molecule creates a deformation of both the molecule and its surroundings. The electronic relaxation channels into vibrational degrees of freedom. The coupling that leads to this will be the same coupling that would lead to a molecular excitation by a mechanically-induced deformation at the site. A deformation energy, $\Phi_{\rm def}$, can be defined for a lattice that is perturbed by compression. The energy change arising from m such perturbed molecules is $\Delta E = mE_0 + \Phi_{\rm def}$. The amount of deformation required to *promote* an electron from the HOMO to the LUMO is $E_0 = \Phi_{\rm def}$ allowing for the fact that, while in a crystal, the HOMO and LUMO are bands which are quite narrow for molecular crystals. Their energies may then be taken as equivalent to the molecular values which leads to $E_0 = I - A = \Phi_{\rm def}$. This is the condition for the electronic instability of the lattice toward deformation and it can be seen that $\Phi_{\rm def} = 2\eta$.

This molecular deformation that is associated with the promotion of the HOMO electron to the LUMO can be determined from the condition for a minimum of the total molecular energy. This allows another expression for the hardness:

$$\eta = \eta_0 - \frac{1}{2}\sum_{\alpha} k_{\alpha}\langle Q_{\alpha}\rangle^2$$

where normal coordinates, Q_{α}, with force constants, k_{α}, are used to describe the deformation.

How is the molecule affected by deformation? The undeformed molecule will have a chemical potential, $\mu_0 = 1/2(I + A)$, and a hardness, $\eta_0 = 1/2(I + A)$). The molecular energy must change upon its deformation, which is reflected in the change in the number of electrons in the frontier orbitals, ΔN:

$$\Delta E = \mu\,(\Delta N) + \eta\,(\,\Delta N\,)^2 + \frac{1}{2}\sum_{\alpha} k_{\alpha}\,\langle Q_{\alpha}\,\rangle^2$$

Because of the deformation, the chemical potential will change:

$$-\left(\frac{\partial\,\mu}{\partial\,Q_{\alpha}}\right)_N = \varphi_{\alpha}$$

as will the molecular hardness:

$$\eta = \eta_0 - \frac{1}{2}\sum_{\alpha}\frac{\varphi_{\alpha}^2}{k_{\alpha}}$$

Modes that describe the molecular deformation will contribute most to the diminution of the molecular hardness.

It has been shown that the instability condition $\eta \to 0$ provides the criterion for the critical distortion necessary for the *mechanochemical* promotion of an electron from the HOMO to the LUMO:

$$\sum_{\alpha} k_{\alpha}\,\langle Q_{\alpha}\rangle^2_{\text{crit}} = (I - A)$$

This promotion can occur before complete closing of the HOMO-LUMO gap leading to a DIMED. It may be viewed as an “inverse” Jahn-Teller effect because its creation is due to structurally relaxed electronic states.

Since hydrostatic stress nominally affects the gap closing, the deformation is due to an imposed shear stress that raises the molecule’s potential energy from the bottom of the potential to the deformation energy, Φ_{def}. The electrons will immediately rearrange according to the deformation with subsequent vertical relaxation to a new state where the molecule is deformed with an electron in its HOMO and one in its LUMO. If the minimum of the potential well of the new DIMED-formed CGS is above the energy of a reactant, relaxation will return the molecule to the reactant state. This will happen when the deformation that occurs cannot compensate for the expense of electronic energy, i.e., $(I - A) > \Phi_{\mathrm{def}}$. However, such relaxation will not occur when the molecule is critically deformed where the molecular state has equally occupied HOMO and LUMO, a condition which is stable. The critical deformation is necessary for the HOMO-LUMO gap "closure." At this point, there will be an electronic energy level with a width designated as $2t$ and a population of 0.5. An insufficient deformation of the molecule forms a non-relaxed HOMO-LUMO degeneracy. Extra deformation energy is required, however, to stabilize the system for it may relax to the unstressed ground state. The energy required to stabilize the CGS must be supplied by cooperative interactions. If $(I - A) < \Phi_{\mathrm{def}}$ then there will be spontaneous creation of CGS molecules. It is these that can do chemistry.

IMPLICATIONS

Mechanochemistry and solid-state chemistry must be synonymous since only solids can suffer shear stress. While most mechanical energy is thermalized and the chemistry that ensues is based on the fate of heat in a chemical process, the direct effect on molecular degrees of freedom by mechanical energy, which will likely be due to compressive forces, may be expected to generate new chemistry.

The simplest process that may be associated with this model is the generation of light when a substance is compressed. Common triboluminescence is attributed to excitation of ambient gas molecules to emit in the presence of high fields created by fissures in crystals. However, another "anomalous" triboluminescence does not correlate with the emission of the ambient gas but apparently inheres in the substance itself. It has been argued that this arises from differences in calibration of instruments, self-absorption or fracture-induced perturbations [15]. However, while the first explanation is certainly independent of the substance and the second is correctable, the third clearly relates to the mechanical properties of the material and may well arise from mechanical excitation to form a CGS which would be capable of emission that differs from the normal excited state of the uncompressed molecule. The local stresses developed by fracture are consistent with a mechanochemical process. The common observation of light emitted from detonating material is also consistent with the mechanochemical model.

Detonation initiation itself is the most obvious example of a mechanochemical process. Because molecules must have higher energy dissociative potentials, there should always be a shear compression of sufficient magnitude to cause mechanochemical mixing of the ground state with a dissociative one. The prediction is that there will always be a sufficiently powerful compression that involves shear that will cause detonation. Thus, barring another process that may cause disintegration of a substance, detonation should always be possible for any material. Reported research on compressively induced detonation of non-energetic materials substantiates this [16]. Even if a stable CGS is created, detonation is a likely event if the system is near the critical deformation energy since but a slight decrease of compression would create an unstable situation and the sudden relaxation to the original state could also be explosive.

More productive from the chemist's viewpoint is the possibility of new chemistry. The CGS is a molecular state that is capable of doing chemistry. It certainly differs from the parent states and suggests that heretofore unexplored chemistry may be available. Just as photochemistry is dictated by the nature of the excited state of a molecule, mechanochemistry will be dictated by the peculiarities of the CGS. The recently developed capability to grow binary crystals [17] suggests that mechanochemical reactions that are other than unimolecular are within reach. However, even study of the reactions of single component crystals may be expected to be fruitful and, combined with DFT calculations, may produce a new area of chemical study.

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