Mechanical Stress and Reactivity in Organic Solids

J. MICHAEL MCBRIDE, BRIGITTE E. SEGMULLER, MARK D. HOLLINGSWORTH, DAVID E. MILLS, BRUCE A. WEBER

Organic single crystals provide an ideal model for studying the factors that influence chemical processes in structured media. Reaction trajectories are well defined and reveal the influence of spontaneous mechanical stresses equivalent to tens of thousands of atmospheres. Analysis of molecular and crystal structures helps to explain both local mechanical properties, which influence reactions, and bulk properties such as melting point, compressibility, and surface energy.

S TUDYING ORGANIC REACTIONS IN MOLECULAR CRYSTALS can reveal their mechanisms in unprecedented structural detail, showing not only the chemical identity of intermediates but also how atoms move through space during chemical transformations. Such studies provide insight into the differences, which are so crucial for biological processes, between reactions in fluids and those in organized media. They also constitute an arena in which organic chemistry can contribute to the solution of problems in materials science, a field that has traditionally been the province of physics and physical chemistry.

One of the principal contributions of organic chemists to solidstate chemistry is an intuition based on the simple mechanical model of molecules and familiarity with the importance of their spacefilling properties and of stereochemistry. These insights have long been an effective qualitative guide to understanding molecular behavior. More recently, computation of molecular structure by "molecular mechanics" has proven them to be quantitatively successful (1).

The mechanical model is also well suited to supply qualitative insight and quantitative information about the behavior of the large molecules and molecular aggregates of interest in materials science and biochemistry. Complex questions of structure, dynamics, and physical properties are already being addressed. These questions involve biomolecules, synthetic polymers, crystals, and even solutions (2).

This article has three themes that relate to understanding solidstate behavior in terms of the mechanics of molecules. (i) An intense stress field appears when reaction intermediates are generated in a solid cavity too small to hold them. (ii) Suitable experiments can give a detailed picture of the influence of this stress on molecules and their motion. (iii) Simple molecular models can be used to explain the stress, its relaxation, and related bulk properties of an organic solid.

Topochemistry, Shape, and Stress

Systematic investigation of reactions in organic crystals began 25 years ago at the Weizmann Institute of Science, Rehovot, Israel, when Schmidt and Cohen inaugurated studies on photodimerization of cinnamic acid derivatives (3). Their efforts were the first of many directed toward explaining product distributions in terms of the structure of the crystalline precursor. They found that the spatial arrangement of atoms in product molecules was similar to that in the starting crystals and that if potentially reactive groups did not make contact in the precursor, the crystal did not react. On this basis they formulated the "topochemical hypothesis," which has guided most subsequent interpretations of solid-state organic reactions. It states that "reaction in the solid state occurs with a minimum amount of atomic or molecular movement" (3, p. 1996).

This hypothesis, which relates results from product analysis to those from x-ray diffraction, was supplemented by Cohen, who suggested that limited motion could occur, but only within the confines of a fixed reaction cavity bounded by supposedly immobile neighboring molecules (4). These ideas make sense in terms of molecular models and have enjoyed widespread success. For example, they are relevant to the solid-state process by which crystalline diacetylenes produce crystalline polymers with unique optical, electrical, and mechanical properties (5). The above ideas are also central to recent detailed investigation of the photochemistry of individual conformers of organic molecules (6). They should also help explain the specificity that characterizes reactions of enzyme-bound substrates.

In other instances, however, more than minimal movement seems to occur. This is most often the case in a mechanism consisting of several steps where an initial exothermic process, perhaps a photochemical one, generates reactive intermediates whose subsequent fate is undecided. Most such transformations involve substantial changes in molecular size and shape, as when bonds are broken so that atom-atom distances must approximately double. When this kind of reaction occurs in a crystal, and there is no possibility that the product molecules would fit into the initial reaction cavity, any reasonable mechanical model predicts that intense local stress fields would be generated. The subsequent chemical and physical behavior of the system should then be dictated as much by the mechanical properties of the environment as by its initial shape (7). In numerous cases, accumulation of such stress causes a crystal to shatter or a reaction to cease (8). This type of response provides a way to probe the microscopic mechanical properties of a solid by

J. M. McBride is a professor of chemistry, Yale University, New Haven, CT 06511. B. E. Segmuller is with Celanese Specialty Operations, Corpus Christi, TX 78469. M. D. Hollingsworth is a postdoctoral fellow in physical chemistry, University of Cambridge, Cambridge, England CB2 1EP. D. E. Mills is with Tennessee Eastman Company, Kingsport, TN 37662. B. A. Weber is a postdoctoral fellow in chemistry, Lehigh University, Bethlehem, PA 18015.

generating a local perturbation that is much more intense than a typical crystal defect.

Computer simulation of solid-state reactions based on the classical mechanical model of molecules should give valuable insight into the roles of shape and stress and the mechanism of stress relaxation. Better understanding of these kinds of mechanically coupled chemical processes will contribute to understanding allosteric effects in biological systems.

A variety of computer models are being developed for simulating reactions in organic crystals (9), but most of our understanding of the role of mechanical stress in solid-state reactions is based on qualitative interpretation of experimental observations. This article describes recent work with long-chain diacyl peroxides; it illustrates the kind of information that becomes available when a variety of physical techniques are applied to a suitably chosen organic system.

A Departure from Least-Motion

Diacyl peroxides, which are readily prepared from carboxylic acids, photolyze to a pair of CO2 molecules and a pair of free radicals, as in scheme 1 (10). The ultimate fate of the radicals in fluid solution is complex and variable, but Feldhues and Schaeffer have shown that photolysis of pure crystals can give a high yield of a radical-radical coupling product (11). A topochemical rationale for coupling is apparent from the crystal packing of diundecanoyl peroxide (UP, the starting material of scheme 1 with R = n-octyl). Since the UP molecule has an extended conformation, the radical pair should be created head-to-head, with each radical confined in a straight, narrow tube. This cage should keep the radicals from separating. If they approach one another, their first contact should be between trivalent carbons. Topochemical least-motion predicts correctly that coupling should predominate both over disproportionation (which requires that one radical abstract hydrogen from the more distant second carbon in the other radical) and over any reactions that require escape from the initial cage (12).



Preliminary comparison of crystal structure with product distribution seems to support the simplest topochemical interpretation, which ignores the role of the new CO_2 molecules. We chose photolysis of UP to allow detailed spectroscopic investigation of the intermediates. We thus avoided the normal requirement of inferring the mechanism from observations at the beginning and the end of a solid-state reaction pathway. The following analysis of the spectra shows that the radicals do not follow a least-motion path toward coupling and shows why. Electron paramagnetic resonance (EPR) is well suited to study the behavior of the radical pair (13), and Fourier-transform infrared spectroscopy (FTIR) is suited to study the CO₂ molecules generated between them (14). In both experiments we used a pure, single crystal of UP to guarantee that the precise initial structure of the reacting molecule and its environment was available from x-ray studies. The crystal was photolyzed at a temperature near 15 K to very low conversion (less than 0.05%), so that the randomly distributed decomposition sites would be independent of one another. Spectra of the intermediates were monitored as the crystal was warmed in stages.

Below 40 K the EPR spectrum of radical pairs from UP is very complex, because there is insufficient motion to average anisotropy of the hyperfine splittings from the four different α - and β hydrogens in each decyl radical. Reducing the splitting by using a crystal in which these hydrogens have been replaced by deuterium gives a much simpler eight-line spectrum. These eight lines occur as four doublets, each due to the magnetic interaction between the odd electrons of a different triplet-state radical pair. The four radical pairs are identical in the sense that they are related by crystal symmetry, but for most crystal mountings they differ in orientation relative to the direction of the spectrometer's magnetic field and therefore in magnetic dipolar coupling.

At 33 K the pairwise structure changes to give a new set of four symmetry-related radical pairs with different doublet splittings. An analogous process at 55 K yields a third radical pair, which, because of higher local symmetry, gives only two doublets. The EPR spectrum finally disappears at 125 K, when the third radical pair collapses to yield products. Partial deuteration showed that the three successive radical pairs (pair A, pair B, and pair C in scheme 2) are chemically identical, differing only in the spatial arrangement of their two decyl radicals and two CO_2 molecules.



Scheme 2

Some investigators who are accustomed to using more energetic radiation and glassy or powdered samples have been surprised by the tidiness of this system. Each intermediate has a single, well-defined arrangement of fragments and converts irreversibly to the next intermediate with ideal first-order kinetics. One might have thought that the reaction fragments would lodge in myriad relative positions, or that "local melting" would destroy the radical pairs, but the pairs are stable at low temperature, and they seem as well ordered in the single crystal as was their precursor molecule.

Zero-field splitting (ZFS) from electron-electron magnetic coupling has been observed in a number of radical pairs, and it was a key tool for detailed mechanistic studies of solid-state carbene reactions by Hutchison *et al.* (15) and by Schwoerer, Sixl, and their collaborators (16). Theoretical interpretation of ZFS is straightforward for the present case because the odd electrons are localized on two reasonably remote carbon atoms (13, 17). In scheme 2 the radicalpair carbon-carbon distances are compared with the analogous distances measured by x-ray diffraction in the starting peroxide and inferred for the coupling product. The reaction does not take a simplistic least-motion path, since the reactive carbons move farther and farther apart before they finally combine.

An obvious source of this departure from simple topochemistry is the stress that is created when two CO_2 molecules appear in a cavity too small to accommodate them. How large can such stress be, and how does the structure of the environment influence the relaxation path? Together with crystal-packing analysis, EPR can answer the second question. Measuring the stress requires a different technique.

The Intensity of Local Stress

The asymmetric stretch mode (ν_3) of CO₂ provides a convenient stress gauge because its frequency responds to pressure (18) and its FTIR absorption is unusually intense. Force along the long axis of CO₂ shortens the bonds. Since the bond stretching is anharmonic, this increases the frequency of ν_3 (19). The band intensity makes it possible with careful experiments to observe even the signals for the CO₂ that contains ¹³C or ¹⁸O in natural abundance.

It is crucial that the gauge be a reaction product, because the stress in question begins as a local phenomenon. Simple analogies from continuum elasticity theory suggest that stress should fall off with the third power of distance from such a point defect (20). As the defect relaxes by inelastic structural changes, the stress should spread and decrease in intensity. Since local stress is highly anisotropic and ν_3 is primarily sensitive to stress along the long axis of CO₂, FTIR gives only a lower limit to the maximum component of stress.

Figure 1 presents the v_3 region of CO₂ spectra from a single UP crystal photolyzed at 20 K and warmed in stages through the temperatures at which EPR spectra showed the intermediates of scheme 2. The correspondence between EPR and FTIR spectral changes confirms that both techniques reveal the dominant reaction pathway. Each intermediate shows a band near 2331 cm⁻¹, which could be taken as normal for CO_2 in this sort of environment, when there is no unusual stress along its long axis. The earlier intermediates (pairs B and A, Fig. 1) show other peaks at progressively higher frequencies, suggesting that they include molecules oriented to receive a longitudinal stress, which decreases with each structural change (21). As in the case of the EPR spectra, the sharp FTIR lines show that relaxation involves discrete transitions between welldefined structures rather than a gradual adjustment of positions. It seems that elastic compliance to the stress is rapid at any temperature, while inelastic adjustments give rise to discrete transitions.

The frequency range for ν_3 in Fig. 1 is about 20 cm⁻¹. If this difference were due to changes in local stress, the maximum stress



Fig. 1. CO_2 asymmetric stretching in the FTIR spectra of a lightly photolyzed crystal of UP, measured at 20 K after successive warming to generate the species of scheme 2. Pairs A and B show four different CO_2 molecules (21). would have a lower limit equivalent to a pressure of 40 to 60 kbar, nearly enough to convert graphite to diamond (22, 23). Other possible sources may, in the aggregate, account for as much as half of the observed spread of frequencies, but we think that stress dominates and is equivalent to at least 20 kbar (14). This amount is greater than pressures that are applied externally to change the course of organic reactions (24). A stress this high, and its anisotropy, may well be as important as initial cavity shape in differentiating solid-state from solution reactions.

How can crystals that are so malleable they bend under their own weight at room temperature tolerate such high stress? An obvious factor is that these studies are conducted at low temperature. A more important one is that stress is confined within a cavity of small radius in an otherwise perfect local structure, free from the defects where failure normally begins. The fragments from a UP molecule should require a cavity with a radius about 10% larger than one built to hold their precursor. Linear elasticity theory suggests that increasing the radius of a spherical bubble in an isotropic material by 10% requires a pressure equivalent to 40% of its shear modulus (20). In biphenyl at room temperature this would amount to about 6 kbar; in xenon at 5°C below its melting point, to 3 kbar; even in plastic cyclohexane at 6°C, to 1 kbar (25). In this context it seems plausible that below 30 K, crystalline UP could confine point defects with pressures of several tens of kilobars. It also seems likely that other two- or three-dimensionally organized media could tolerate chemically significant stress, until there is a discrete, inelastic structural change.

The Relaxation Pathway

How the stress relaxes is as relevant as its initial magnitude. Analysis of the crystal packing for UP suggests how the defect should expand to relieve pressure on the CO_2 molecules. The long, narrow UP molecules bulge at the center, where carbonyl oxygen atoms project from the main chain. Figure 2 shows that the polymethylene chains tilt relative to the plane that contains molecular centers, so that, sliced on the bias, their cross-sectional area can approach the cross-sectional area near the molecular center and give reasonable overall packing efficiency.

It is not possible, however, to pack the chain ends tightly. The even number of methylene groups in the tilted, zigzag chain requires the last C–C bond to stand almost perpendicular to the layer plane. Since the terminal methyl carbon is unique in having no bonded neighbor in a direction parallel to the layer plane, the molecular cross section at the chain ends is unusually small. The intermolecular space is correspondingly large in this region, but it is insufficient to allow appreciable interdigitation with the ends of chains from the adjacent layer, so excess free volume accumulates at the layer interface.

One can visualize the distribution of free volume in the crystal quantitatively by plotting a profile of the fractional free area of a plane parallel to the interface against the distance of the plane from the interface (26). Figure 3 contrasts the distribution for UP with that for crystalline octadecane, a typical straight-chain hydrocarbon. It is apparent that UP has little free volume near the molecular centers, typical polymethylene density through the chains, and unusually large free volume at the chain ends. Compressibility should be high in the interlamellar region and low near the peroxide groups. Stress generated by peroxide cleavage in the densely packed heart of the layer should relax through the motion of molecules toward the interface.

In the procedure discussed above we used the doublet splitting in the radical-pair EPR spectra to measure the distance between radical carbons. Measuring the ZFS as the crystal orientation is changed gives the direction of this vector, since splitting maximizes when the vector is parallel to the applied magnetic field. One can thus measure relative carbon positions to within about 0.2 Å (17). This information is interpreted in terms of absolute positions in Fig. 4. Analysis of the anisotropy of hydrogen hyperfine splitting for pair C, in which there is rapid rotation about the first C–C bond in each radical, establishes the direction of these bonds and thus the positions shown for the second carbon in each chain.

In forming pair A only one radical moves. This motion breaks the local symmetry and begins to accommodate the two new CO₂ molecules. During subsequent relaxation to pair B the same radical moves its first carbon, the trivalent one, to the position that had been occupied by the second alkyl carbon in the undamaged UP molecule. At the same time the second carbon replaces the third, and it seems likely that each successive carbon replaces its neighbor, except the terminal methyl, which must be driven into the interface. In forming pair C, the other radical in the pair is driven back in an analogous 180° rotational translation. These screw motions transfer stress from the crowded center of the layer to the low-density interface, while preserving the packing pattern of the zigzag chain. Since motion of the first radical of a pair reduces the stress that must also serve as the driving force for motion of the second radical, it is natural that the latter motion, although identical to the former, occurs only at a much higher temperature. This screw motion may be the most direct experimental example of the kind of longitudinal chain diffusion that is proposed for crystalline alkanes and for polymer relaxation by the reptation mechanism proposed on theoretical grounds by de Gennes (27).

FTIR spectra can supply additional geometric detail on the motion that accompanies relaxation (14). For example, polarized FTIR spectra give the orientation for most of the CO₂ molecules to within about 5°. Comparison of the frequency and intensity of ¹³CO₂ bands with those shown in Fig. 1 allows measurement of the extent to which vibrations of the CO₂ molecules in a pair are coupled with one another. The dominant coupling mechanism is electrostatic interaction of the transition dipoles of the vibrating CO₂ molecules. This electric dipole coupling is closely analogous to magnetic dipole coupling of the radical pair, which gives ZFS in the EPR spectrum. The magnitude and sign of the vibrational coupling constant are related to the distance and direction between the CO₂ molecules.

The combined geometric information from EPR and FTIR spectra is considerable, but it is insufficient to determine the precise arrangement in space of the four reaction fragments in each stage of relaxation. Efforts are under way to simulate the intermediate structures, and the low-energy paths among them, by using molecular mechanics calculations (28). The spectroscopic data should confirm correct calculations and exclude others.

The Use of Substituents

Although results of computer simulations are not yet available, the proposal that stress is relaxed by rotational translation of the decyl radicals has been confirmed by using substituent effects.

The proposed mechanism assigns a unique mechanical role to the chain terminus, which is nine C–C bonds removed from the reaction center. The mechanism was tested both by replacing the terminal hydrogen with chlorine, bromine, and iodine and by replacing the terminal methyl with hydrogen. The halogenated UP molecules are packed in layers that are isostructural with those of UP, except that halogens fill the voids between terminal methyls to give tighter interlayer packing. As expected, radical pairs in these chains do not



Fig. 2. Crystal packing of UP viewed along a, the shortest axis of the C222₁ unit cell. Filled circles denote oxygen. Molecules drawn with heavy lines lie in grooves formed by their nearest neighbors, which lie behind them and are drawn with light lines. The central layer is related to those above and below by a vertical twofold screw axis and by horizontal twofold screw axes between the layers, which allow methyl groups to mesh across the interface.

back up by the twofold screw motion. Kept from moving backward or forward, ω -halogenated radical pairs survive to higher temperatures than those from ordinary UP. The radicals ultimately attack neighboring molecules to initiate chain reactions that convert radical pairs into isolated radicals (29).

Replacing the terminal methyl by hydrogen involved preparing a single-crystal solid solution of UP containing 12% of its unsymmetrical homolog with one chain shortened by one carbon. In a sense these solute molecules have a terminal hole as a substituent. In order to monitor behavior of the defective molecules by FTIR, we labeled their CO₂ groups with ¹³C, which distinguished them from the more abundant CO₂ from the photolyzed host. As expected, sites with extra space at the end of one chain relaxed much sooner than sites involving two normal chains (*30*).

These examples demonstrate the use of remote substituents to investigate the mechanics of a solid-state reaction. Substituent effects have been a powerful tool for studying solution reactions. But these effects are more difficult to interpret in solids, because a change of substituent normally alters crystal packing so drastically that it is difficult to determine which aspect of the alteration influences the process in question. For example, photolysis of crystalline UP gives a significant yield of heptylcyclopropane (12), but photolysis of crystalline lauroyl peroxide in which each alkyl chain is one carbon longer than in UP gives none of the homolo-



Fig. 3. Distribution of free volume in crystal layers: solid line, UP; dashed line, octadecane. Filled diamonds and circles mark carbon positions; open circles, oxygen. UP packing is unusually tight near the oxygens, loose near the interface.



Fig. 4. The central portion of undamaged UP with filled diamonds and circles indicating the positions to which various carbon atoms in the successive radical pairs have been driven by the new CO₂ molecules. Open circles indicate oxygen atoms of UP. Diamonds indicate positions for the first alkyl carbons (the radical centers), and filled circles indicate positions for the adjacent carbons, when known. Radical positions were established by EPR spectroscopy. In pair C both radicals have recoiled by a screw motion, in which each CH₂ takes the position that the adjacent CH₂ occupied in the starting molecule. In pairs A and B only one radical has moved.

gous cyclopropane. This difference may not be due directly to the influence of the extra carbon at the chain terminus, but rather to the different arrangement of neighboring molecules in crystals of the homologous peroxide.

Substituent effects on UP from ω -halogenation or from deliberate introduction of a hole defect are easier to interpret, because x-ray diffraction shows that they do not substantially alter crystal packing in the vicinity of the reacting group. This structural similarity allows the investigator to focus attention on the interfacial region where the structures differ. The search for an explanation can thus be limited to a single plane rather than ranging over the whole volume of the crystal. In a sense this simplifies the search from three dimensions to two.

Relating Molecular Structure to Bulk Properties

The success of interpreting local stress relaxation in terms of packing at the layer surface suggests the existence of analogous structural explanations for bulk properties of the crystals. One such property is the melting point. Few regularities of nature are simultaneously so widely recognized and so poorly understood as the odd-even alternation in melting point of various long-chain compounds, where plots of melting point against chain length give a different smooth curve for each parity (31). Often the difference in symmetries available to compounds having odd and even numbers of carbon atoms has been proposed as an explanation. Such differences can restrict the odd and even series to different space groups, so that they should behave differently, but a more satisfying explanation would tell which parity melts at a higher temperature and would identify the particular interactions that cause the alternation. Because packing is so different between the two series, it is difficult to identify the key discriminant.

The long-chain diacyl peroxides show melting point alternation, with those derived from odd-carbon acids melting at a lower temperature than those derived from even-carbon acids (12). Because the overall molecular chain is of even parity for both peroxide classes, there is no symmetry-based reason that even-acid homologs of UP could not pack with the same layer structure and space group as UP. In fact, however, they pack quite differently, which again foils attempts at correlating structure with melting point.

The terminally brominated peroxides also show melting point alternation, with terminally brominated UP (11-BrUP) in the highmelting series (29). X-ray diffraction has shown that low-melting UP and high-melting 11-BrUP differ in structure only at the layer interface. It seems more than coincidental that low-melting UP has gaps at the interface that allow decyl radicals to be driven into the region by CO₂ pressure, whereas high-melting 11-BrUP differs in structure only in the tight packing at the interface, which resists such motion. Attraction across the interface should be stronger for tightly packed layers, and it provides a plausible link between melting point elevation and lattice rigidity (32).

If packing density at the layer boundary affects local compressibility, it should also influence thermal expansion of the crystal in the direction normal to the layers. Variable-temperature x-ray diffraction of UP shows that from 130 K to room temperature the spacing between molecules within a layer increases by 0.07 Å, whereas the spacing between layers increases by 0.54 Å. For 11-ClUP, the chlorinated analog, the corresponding figures are 0.07 and 0.20 Å. Expansion within the layer is insensitive to chlorination, but expansion between layers decreases threefold. Most of this difference is probably due to filling voids at the interface, and not simply to the increased van der Waals attractiveness of chlorine, because the brominated and iodinated analog show about the same expansion at 11-ClUP.

If structure at the layer boundary is so influential within the crystal, it should also be important at the crystal surface. This possibility suggests attempting to correlate surface properties of individual facets of organic single crystals with the molecular and crystal structure. Of course, the structure of a layer surface at the solid-air interface could differ from its structure within the crystal. For example, one might imagine that in the absence of methyl groups from the opposing surface, the terminal C-C bonds of UP would turn to consolidate the surface layer. In inorganic systems where good physical techniques exist for determining atomic structure at surfaces, gross differences from bulk structure have been observed (33). These techniques are generally inappropriate for lowenergy surfaces of unstable, low-melting organic insulators. Measurement of contact angles at the solid-liquid interface, although a relatively simple technique, is both applicable to such materials and sensitive to the nature of the immediate surface (34). These measurements are directly relevant to questions of adhesion and lubrication, and structure at the solid-liquid interface may be more similar to that at the solid-solid interface than structure at the solid-air interface is.

The contact angle between a liquid drop and a planar, solid surface reflects competition between the liquid's cohesion, which tends to give a bead with a high angle, and its adhesion to the solid, which tends to make the drop spread and give a low angle. Measuring the angle for a liquid of known surface tension yields the energy of adhesion. Although the experimental contact angles for the peroxide crystals are subject to considerable uncertainty (35), they show the relation between the structure of the surface and its adhesive power (36).

On the layer surface of tridecanoyl peroxide (TP), which, like UP, has dangling methyl groups, the advancing contact angle of methylene iodide is 74°, much closer to the 88° on Teflon than to the 52° on polyethylene (37). Teflon appears unattractive because of the fluorines and TP because of the prevalence of empty space in the surface layer. The corresponding angles for chlorinated, brominated, and iodinated UP are 40°, 31°, and 32°, respectively. All halogens appear to increase adhesion by filling the spaces, with bromine and iodine giving stronger van der Waals attraction than chlorine.

With 1,2-propanediol as the liquid the contact angle on TP (72°)

is again high, while those on the halogenated UP's are lower (chlorine, 55°; bromine, 56°; iodine, 57°). The similarity among the halogen values presumably reflects offsetting changes in van der Waals attraction and in hydrogen bond strength (36).

Prospects

For mechanistic organic chemists, single crystal reactions have unique appeal, because they show promise of revealing the trajectory of complex molecular transformations in atomic detail. Only computer simulations of metastable structures and transition states can presently provide this kind of ultimate detail. Experiments like those discussed above show that pathways are sufficiently well defined to be worth simulating. They also give a qualitative idea of what influences are important for reaction. An increasingly important contribution of experiments will be to provide a variety of quantitative geometric and kinetic criteria for identifying accurate simulations.

Such detailed mechanistic information will be valuable to the extent that it yields new insight and generalization about the factors that control reactions in structured media and in solution. The inference that reaction-generated mechanical stress is important for ordered, rigid media should be tested for generality in systems that are disordered or fluid. It is not obvious whether the distinction between rapid elastic and slow inelastic relaxation will apply in the same way to reactions in less highly ordered or glassy media. Since relaxation is a question of time scale, it is possible that analogous mechanical stress could be important even in solution for very rapid processes.

If solids can be useful for studying reactions, the converse is also true: reactions provide a convenient probe of a solid's mechanical properties at the molecular level, particularly when they generate products whose spectra are sensitive to the properties.

Other families of crystals in which, as in these peroxides, chemical substitution can give a purely local structural change should prove equally valuable for understanding the relation between molecular structure and various bulk properties and for tailoring crystal properties. Recent advances in rationally controlled growth of organic crystals promise to facilitate this type of research by making suitable crystals more readily available (38).

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