Mechanochemistry

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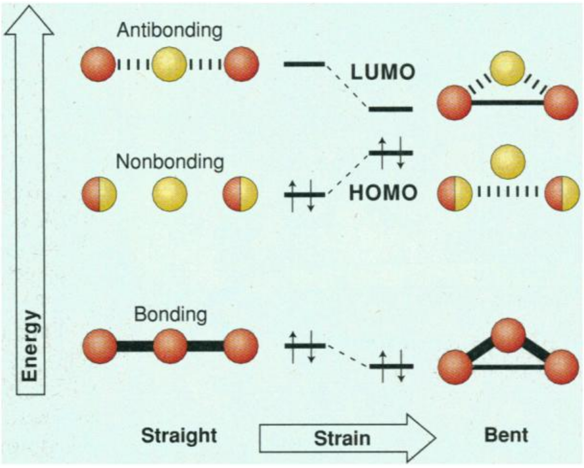
Chemical reactions can be triggered by mechanical forces in solids because, unlike gases and liquids, solids support shear strains. Shear changes the symmetry of a molecule or solid and is therefore more effective in stimulating reactions than is simple isotropic compression. Sheared spheres become ellipsoids, cubic symmetry becomes tetragonal, and so on. Such symmetry breaking destabilizes the electronic structure of bonding and makes the solid prone to chemical reaction. Such mechanochemical phenomena are found in a variety of processes—friction and wear, detonations, solid-state synthesis, and mechanical alloying.

Boldyrev (*1*) has emphasized that products of mechanochemical reactions may be distinct from those of thermochemical ones for the same reactants. Until recently, there was a great deal of phenomenological knowledge in this field but no satisfactory knowledge of mechanisms.

Bridgman (*2*) reported in 1935 that he could cause a variety of chemical changes by applying a combination of axial compression and torsion to specimens held between two "Bridgman anvils" at room temperature. Under about 50 kbar of compression (plus torsion), he could cross-link polymers, decompose compounds such as PbO and $KMnO_4$, and drive substitution reactions such as $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$ and $Mg + SiO_2 \rightarrow MgO + Si$. Because his specimens were thin wafers and his anvils were good thermal conductors, he concluded that the reactions were athermal.

Enikolopyan *et al.* (*3*) extended Bridgman's work to various inorganic compounds, such as hydrated cupric sulfate, and to the polymerization of various organic monomers (those containing –C=C–, –C=N–, C≡C, C≡C≡C, and heterocyclic and aromatic groups). Hundreds of such mechano-reactions are reviewed by Zharov (*4*). Studies of acrylamide have demonstrated that polymerization occurs principally during the shear deformation, not afterwards.



How strain triggers chemical reactions. Walsh energy-level diagram for H_3^- showing the effect of bending shear on the LUMO-HOMO gap. Occupation of the levels is indicated by the small arrows, which represent spin-up and spin-down electrons. There are three protons and four electrons. The phases ϕ of the electronic wave functions are indicated as yellow for $\phi = 0$ and as red for $\phi = \pi$. Neighbors with like phases bond; unlike ones antibond. Mixed (half-shaded) ones do neither.

Mechanochemical effects have often been attributed to strain energy assisting thermal energy. However, at low temperatures, the strain energy density may be larger than the thermal energy density, so this assumption is inappropriate. In many cases, dislocation motion concentrates the applied strain, creating large local strains (*5*).

When covalent bonds are bent (sheared), the energies of their highest occupied molecular orbitals (HOMOs) are raised, whereas the energies of their lowest unoccupied molecular orbitals (LUMOs) are lowered. Thus, the gap between these levels, which determines a bond's stability, is decreased (*6*). This may be viewed as an inverse Jahn-Teller effect.

Consider the simplest case: the hypothetical H_3^- molecule, which is related to the azide ion N_3^-. A Walsh diagram indicates the molecular orbital energy as a function of bond angle (see figure). Such a diagram shows that like pairs with in-phase wave functions form bonds, whereas unlike pairs form antibonds.

For the bent molecule on the right, the lowest orbital (bonding orbital) is stabilized by increased bonding between the two end atoms. This interaction increases for the antibonding orbital, thereby lowering its energy, and decreases for the nonbonding orbital, so its energy increases. Work is done on the molecule to bend it, thus the total energy rises, but the LUMO-HOMO gap decreases, and so the internal stability decreases. As a result, there is a greater opportunity for chemical reactions to take place. If a molecule is bent in its ground state, straightening it decreases its stability.

In periodic solids (crystals), the equivalents of LUMO-HOMO gaps are band gaps. Bonding orbitals correspond to valence bands; and antibonding orbitals, to conduction bands. The larger the band gap, the more stable the crystal structure (*6*). For example, there are two mechanical paths for converting insulators into metals. One, the Herzfeld-Mott approach (*7*), reduces distances between atoms so that the overlaps of their wave functions increase. The other changes the bond angles through shear, thereby reducing the minimum band gap (*8*).

A simple two-dimensional model that compares the effects of shear versus isotropic compression on the electronic structure provides some insight (*9*). By shortening one axis while lengthening the other, shear shifts two band gaps oppositely in energy, whereas isotropic compression shifts them in the same direction. Thus, the minimum (indirect) gap is decreased by shear but is nearly unchanged by isotropic compression. Band structure computations of 3D molecules are consistent with this simple model (*10*).

When the strain becomes large enough to close the gap, the bonding electrons can move freely, so that a transformation, or reaction, can proceed athermally. In intermediate cases, the electronic process may be assisted by phonons, allowing reactions to occur very rapidly at low temperatures because of its electronic basis. Mechanochemistry is especially important for ultrafast reactions, as in explosive shock fronts. It accounts for the transitions between deflagrations that travel at sonic speeds and detonations that travel supersonically through a solid. The former are thermally activated, whereas the latter are athermal (*11*).

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