Covalent Chemomechanics for Materials Design.

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Chemomechanics is an emerging field at the interface of chemistry, materials science, physics and biology focused on understanding how chemical reactions respond to forces that develop when molecules are distorted. Reaching far beyond the early foundations of molecular-strain studies, chemomechanics exploits the size-invariant nature of force to allow quantitative understanding of energy coupling in the "formidable gap" between 10 and 100 nm, where the molecular meets the bulk. Examples of chemomechanical phenomena range from operation of motor proteins, to mechanosensing, to behavior of materials during crack propagation or at interfaces, to reactions in shear flows, to molecular actuation. Chemomechanics forms the conceptual framework to guide the design of new materials and processes for molecular-level control of energy flows across length scales, including "artificial muscles" for efficient conversion of chemical or light energy into directional motion on the microscale and materials capable of autonomous molecular-scale damage-sensing and self-repair.

Realization of the full potential of the chemomechanics requires general, quantitative and predictive models that relate restoring forces, reaction rates, molecular structures and reaction mechanisms. Such models are lacking. Reactions of strong (covalent) molecular bonds within small (<1 nm) moieties are most promising for understanding the fundamental aspects of chemomechanics and are easiest to exploit in creating materials to direct chemomechanical energy flows. Yet chemoechanics of such reactions has been little studied because they are largely "invisible" to the existing methods of controlling molecular restoring forces. We recently developed a general strategy to overcome such limitations by relying on molecular design instead of micromanipulation techniques to generate restoring forces up to 600 pN in diverse reactive groups with sub-Å positional accuracy and in <30 pN increments (*Nature Nanotech*. **2009**, *4*, 302). Our strategy allows systematic studies of force-dependent kinetics and reaction mechanisms of diverse molecules by embedding them in inert 10-20 atom straps stretched across a rigid hydrocarbon, stiff stilbene, which acts as a molecular force probe.

We have used this approach to (1) validate the key assumption of modern chemomechanics for 8 mechanistically diverse reactions and to develop general rules for identifying a pair of atoms whose motion during the reaction accounts for most of the strain-induced kinetic perturbation; (2) identify the molecular basis of the breakdown of the standard chemomechanical model for the simplest examples of multi-step reactions and to modify the model to treat such reactions; (3) test the validity of the widely discussed hypothesis that rates at which covalent bonds break are sensitive only to restoring force along the bond; (4) develop and benchmark the accuracy of a general quantum-chemical approach to explicitly calculate force-rate correlations.

Our current goals are on understanding chemomechanics of reactions for advanced polymers, with particular focus on measuring and rationalizing structurally and mechanistically how force affects rates of reactions that results in changes in molecular shapes (such as thermal and photo isomerizations of C=C and N=N bonds) and of reactions that yield colored, fluorescent or highly-reactive products. By studying these specific reactions we continue to acquire key empirical data (force-dependent kinetics and its sensitivity to substituents) and to create interpretational tools (general chemomechanical kinetic models and methods for direct quantum-chemical calculations of force-rate relationships) to (1) assist the design of actuating polymers with practical efficiencies of photomechanical energy conversion; (2) enable simple, accurate colorimetric measurements of local internal forces in polymers under mechanical loads, in sheared flows and other anisotropically stressed environments; and (3) identify reactions which, driven by dissipation of large-scale deformation energy in a mechanically stressed material, can rapidly cross-link this material around incipient cracks to prevent its failure. We believe that this data will contribute to solving one of the key Grand Challenges of modern science: precisely controlling energy flows across multiple length scales.