Chemomechanics with a Molecular Force Probe

Zhen Huang Final Seminar May 13, 2010

Chemomechanics is an emerging area at the interface of chemistry, materials science, physics, and biology that aims at quantitative understanding of reaction dynamics in multiscale phenomena.[1-6] These are characterized by correlated directional motion at multiple length scales—from molecular to macroscopic. To explain the up to 10^{15}-fold variations in reaction rates in multiscale phenomena—which are incompatible within the standard models of chemical kinetics—chemomechanics relies on the concept of molecular restoring force. We developed a general framework of force-dependent kinetics from the normal mode formalism, and simplified it in the form of Taylor expansion (eq. 1).[2]

$$\underbrace{\ln k_f = \ln k_o + \frac{\partial \ln k}{\partial f} f}_{1st\ order\ Taylor\ expansion} + \underbrace{\frac{1}{2}\frac{\partial^2 \ln k}{\partial f^2} f^2 + \sum_{n=3}^{\infty} \frac{1}{n!}\frac{\partial^n \ln k}{\partial f^n} f^n}_{2nd\ order\ Taylor\ expansion} \qquad (1)$$

Molecular force probes are inert molecules that allow incremental variations in restoring forces of diverse reactive moieties (Figure 1).[2,7-11] Extending beyond the classical studies of strained molecules,[12] they enable experimental explorations of how restoring force affects chemical reactivity. In this presentation I will describe the utility of one such broadly useful probe—stiff stilbene. Various reactive moieties were incorporated in inert linkers that constrained stiff stilbene to highly strained macrocycles. Such series eliminated many constraints of conventional microscopic force probe, provided direct experimental validation of Taylor expansion (Figure 2)—a generic form of the most popular chemomechanical model[5,13]—and illustrated the diversity and predictive capabilities of relationships between reaction rates and forces and their potential in guiding the design of novel stress-responsive materials.

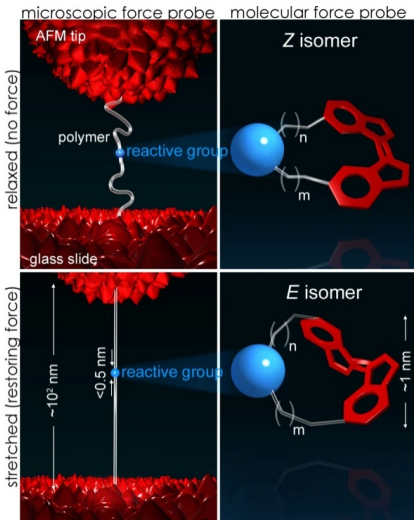

Figure 1. A schematic comparison of force spectroscopy of localized reactions with microscopic (red, left) and molecular (red, right) force probes.[7]

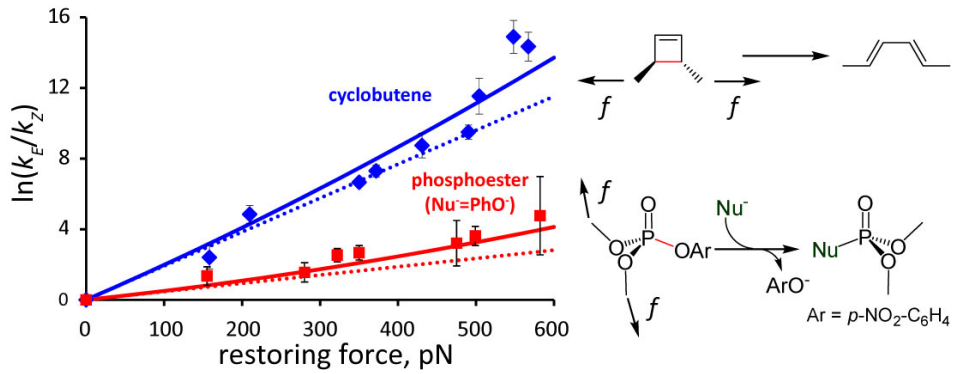

Figure 2. 2nd-order Taylor expansion (solid lines) predicts well force-dependent kinetics of the C-C scission in cyclobutene (blue) and the P-O scission in phosphoester (red) whereas 1st-order Taylor expansion (dotted lines) underestimates at high forces. Scissile bonds are in red.

The reverse process, how chemical reactions may generate restoring force and useful mechanical work through directional motion across multiple length scales, remains much less understood.[14-16] I will describe a simple operational model to relate the key features of a photoactuating polymer to the force-dependent kinetics of the actuating and side reactions of its monomer.[17] Experimentally measured kinetic parameters for both photo- and thermal isomerizations of the C=C bond in series of stiff stilbene macrocycles as a function of its restoring force (Figure 3) allow systematic optimization of the operating conditions, and suggest its maximum attainable performance is comparable to what motor proteins offer. This conceptual framework highlights the opportunities in rational design of photoactuating polymers afforded by the concept of restoring force.

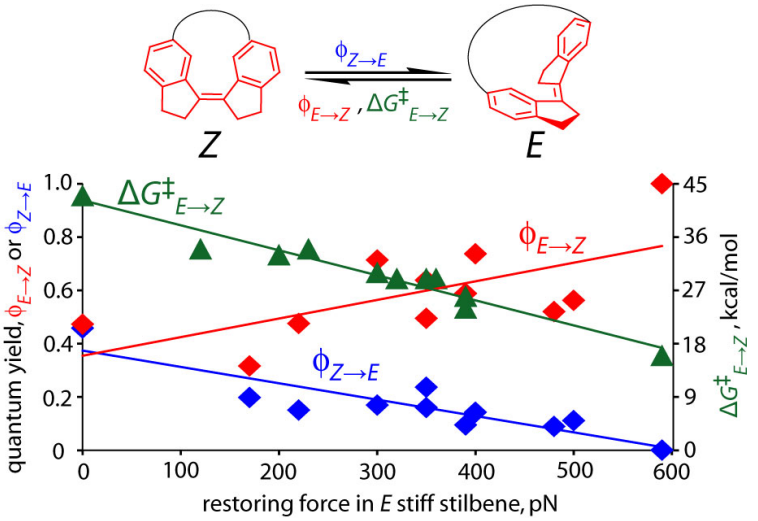

Figure 3. Force-dependent kinetics of both photo- (blue and red) and thermal (green) isomerizations of the C=C bond allows the limiting performances of a photoactuating polymer to be estimated.[17]

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