

NORTHWESTERN INSTITUTE ON COMPLEX SYSTEMS PRESENTS

Wednesdays

@NICO

Complex Reaction Networks: Analysis and Discovery

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Wednesday, November 5th, 2008

12:00 – 1:00 PM

Chambers Hall, 600 Foster Street, Lower Level Classroom

We have developed methods for automated generation of reaction mechanisms of complex systems that allow kinetic models of substantive detail to be built. Molecules are represented as graphs and matrices, and operations on these representations allow reaction to be carried out, molecule uniqueness to be determined, and properties to be calculated. We have applied our methodology to a wide range of different problems, including production of silicon nanoparticles, biochemical transformations, polymerization and depolymerization, and tropospheric ozone formation. While the chemistries we have studied are seemingly very disparate, applying a common methodology to study them reveals that there are many features of complex reaction networks that are ubiquitous.

This presentation will focus on two of the systems we have examined: aromatic amino acid biosynthesis and tropospheric ozone formation. For the first system, a computational framework has been developed for the construction and evaluation of metabolic pathways given input substrates and knowledge of enzyme-catalyzed reactions and applied to study pathways to aromatic amino acids. Application of the framework creates new and existing routes to both chemicals known to exist in biological systems and chemicals novel to biological systems. The concept of generalized enzyme function is introduced and defined as the third-level enzyme function (EC i.j.k) according to the four-digit transformations of the enzyme classification system (EC i.j.k.l). This concept maps enzyme-catalyzed reactions to transformations of functional groups and enables the generation of novel species and pathways. Thermodynamic properties are calculated using a group contribution method “on-the-fly” in order to provide one assessment of the relative feasibility of the novel pathways.

The second system focuses on formation of ozone, a major component of photochemical smog, from volatile organic compounds (VOCs). While it is known that different organics in the atmosphere vary in their reactivity and thus their contribution to ozone formation, it would be extremely valuable to have the ability to determine how significantly a particular VOC contributes to ozone formation. A promising strategy is to assemble knowledge of the kinetics and photochemistry into detailed mechanistic models from which predictions of ozone concentrations may be obtained. To date, only lumped models have been created because of the size of the implied models and the lack of rate constant data. To overcome these challenges, automated mechanism generation has been applied. Thermal and photochemical reaction families were identified and implemented. A group additivity approach similar to the one developed by Benson to estimate thermodynamic data was developed to estimate absorption cross sections over the wavelength region of tropospheric interest. Mechanisms were then generated automatically for various systems using different criteria for halting generation to control the explosive nature of the chemistry. A range of VOCs was investigated, including formaldehyde, acetaldehyde and acetaldehyde/alkane mixtures. The models were compared to experiments carried out at various NO_x concentrations, and it was observed that the models were able to extrapolate well to different conditions.

NICO Coffee Hour will follow for questions, networking, and collaboration.

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