

Spotlights on Recent JACS Publications

■ PREDICTING THE RATES OF TUNNELING BY CARBON IN CARBENE REARRANGEMENT REACTIONS

Quantum mechanical tunneling by hydrogen is ubiquitous in both chemistry and biology. Although carbon tunneling is a much less common process, it can play a critical role in some organic reactions, particularly when the reactions are carried out under cryogenic conditions.

Sebastian Kozuch, Weston T. Borden, and co-workers have used quantum chemical calculations that include the effects of tunneling in order to compute the rate constants for the ring expansion reactions of some strained cyclic carbenes (DOI: 10.1021/ja409176u). The authors validate their computational methodology by comparing the rate constant calculated for one such reaction with that determined experimentally at 9 K. The authors then predict that the effect of mass on tunneling rates should change the course of the rearrangement of noradamantylmethyl carbene from carbon migration at room temperature to hydrogen migration at low temperature. The change in the predicted product constitutes an example of how tunneling can completely alter the course of a chemical reaction.

This study not only provides calculated rate constants for some carbon and hydrogen tunneling reactions, but it also makes predictions that can be tested experimentally. In addition, this paper furnishes experimentalists with some qualitative theoretical guidelines to the factors that control the rates of tunneling reactions.

Xin Su, Ph.D.

■ BRINGING AN ANTIBIOTIC-MAKING MACHINE TO LIFE IN THE LAB

For the first time, Chaitan Khosla and colleagues have reconstituted *in vitro* a member of an important family of enzyme complexes that produce antibiotics and other molecules of therapeutic interest (DOI: 10.1021/ja409048k).

Polyketide synthases are multidomain enzyme complexes found in bacteria, fungi, plants, and some animals. They produce polyketides, a class of compounds that includes valuable antibiotics such as tetracycline and erythromycin and the anticholesterol drug lovastatin.

But because of the complexity and large size of these enzymes, it has been challenging to reconstitute them *in vitro* from purified protein components. Now Khosla and co-workers have accomplished this task by expressing the components of type 1 polyketide synthase in recombinant strains of *Escherichia coli*, purifying them, and reconstituting them into a complex. The work could enable the bioengineering of similar polyketide synthases to produce therapeutic compounds and illuminate how this important protein complex makes metabolic products.

Deirdre Lockwood, Ph.D.

■ A SWEET APPROACH TO SERS-BASED GLUCOSE DETECTION

Glucose sensors play a critical role in the monitoring and treatment of diabetes, which affects 382 million people worldwide. For the first time, researchers led by Weng Kee Leong and Malini Olivo use surface-enhanced Raman spectroscopy (SERS), in conjunction with a novel organometallic probe, to detect glucose in a spiked urine sample (DOI: 10.1021/ja409230g).

The researchers fabricate a SERS-active substrate and attach a boronic acid-containing molecule that behaves as the primary carbohydrate receptor. They then introduce a sample containing glucose, fructose, or galactose, followed by a transition metal carbonyl probe that binds preferentially to the immobilized glucose and enables detection via SERS. The approach is compatible with glucose detection in biological samples because the spectral window used for glucose quantification (1800–2200 cm^{-1}) has little interference from functional groups present in biomolecules, the researchers say.

The team uses the sandwich assay to accurately detect glucose in a human urine sample doped with glucose. The authors believe that the method's advantages over other glucose assays—no need for sample purification, extremely low sample volume requirement, and very high specificity for glucose—make it a promising candidate for development into a clinical diagnostic tool.

Christine Herman, Ph.D.

■ PROBING THE PATHWAYS OF POTENT POLYMERIZATION CATALYSTS

Eugene Y.-X. Chen and colleagues clarify the mechanisms of an intriguing set of organic catalysts that mediate single addition, dimerization, and polymerization reactions, including one that can be used to rapidly produce bioplastics (DOI: 10.1021/ja4088677).

A class of organic catalysts known as N-heterocyclic carbenes (NHCs) are stable and yet highly reactive and selective in promoting a variety of polymerization reactions. One promising application of these catalysts is the production of sustainable chemicals and biofuels from biomass-derived compounds. Recently, researchers have discovered the first NHCs that can, on their own, initiate the rapid polymerization of acrylic monomers through conjugate addition.

Now the authors have investigated the mechanisms of catalysis of three of these NHCs using experimental and computational methods. The team explores the selectivity of different NHC structures for catalyzing reactions including enamine formation, dimerization, and polymerization. Notably, one of the NHCs polymerizes 10,000 equivalents of a biomass-derived cyclic acrylic monomer quantitatively within 5 min to produce a bioplastic. The study could enhance applications of these catalysts for rapid production of renewable bioplastics.

Deirdre Lockwood, Ph.D.

Published: November 22, 2013