

## Spotlights on Recent JACS Publications

### ■ MOLECULAR CATALYST STABLE AT LOW PH FOR HYDROGEN EVOLUTION

Jenny Yang and Charlene Tsay report a rare example of a molecular catalyst for hydrogen evolution that is highly stable in acidic aqueous environments (DOI: [10.1021/jacs.6b05851](https://doi.org/10.1021/jacs.6b05851)).

Hydrogen is expected to play an important role as a fuel, energy carrier, and energy storage medium in future green energy systems. It is not readily available in pure form, and its production requires energy. A sustainable and environmentally friendly way to produce hydrogen is through the hydrogen evolution reaction, a process that takes place in electrolytic cells to split water into hydrogen and oxygen. Current electrolytic cells favor highly acidic conditions; however, electrocatalysts that function under these conditions are lacking. Yang and her colleague report a nickel-based molecular catalyst that is stable at low pH. Moreover, the stability of this catalyst permits the researchers to perform a detailed mechanistic study of the catalytic pathways of hydrogen evolution. The insight gained may facilitate future design of new and more efficient catalysts for hydrogen evolution.

Alexander Hellemans

### ■ UNPRECEDENTED UPHILL THERMODYNAMICS FOR A RIBONUCLEOTIDE REACTION

Daniel Nocera, JoAnne Stubbe, and their colleagues unveil the unlikely thermodynamic landscape behind a reaction critical for the synthesis of DNA (DOI: [10.1021/jacs.6b08200](https://doi.org/10.1021/jacs.6b08200)).

Ribonucleotide reductases convert ribonucleotides to all the deoxynucleotides required for DNA synthesis and repair. The first step in this reduction reaction is an oxidation that occurs over a distance of 35 Å, a separation that might typically preclude any reaction. To investigate the details behind this unusual step, Nocera, Stubbe, and co-workers in separate experiments replace two critical tyrosine residues in the enzyme with fluorotyrosines and then analyze the thermodynamics of the oxidation using electron paramagnetic resonance spectroscopy.

They show that the thermodynamic landscape of this oxidation is uphill by >200 meV—an unprecedented cliff face, biologically speaking. The researchers suggest that a reaction with this surprising thermodynamic hump may have evolved because it helps the enzyme keep kinetic control over the initiation of the reduction process and prevents radical intermediates from accumulating and causing enzyme self-inactivation.

Deirdre Lockwood, Ph.D.

### ■ STERIC EFFECTS CLARIFIED FOR HAMMETT ANALYSIS

The Hammett analysis has widespread use in physical organic chemistry as a tool to quantitatively describe substituent effects on the chemical reactivity of aromatic compounds, providing insight into the relationship between structure changes and reaction outcomes. While the Hammett values—parameters dominated by electronic effects—are widely applicable in cases

of *meta*- and *para*-substituents, they fail to characterize *ortho*-effects due to the additional steric considerations.

To address this limitation, Matthew Sigman and co-workers use multivariate analyses to develop a comprehensive method that can account for all types of substituent effects, particularly *ortho*-steric effects (DOI: [10.1021/jacs.6b08799](https://doi.org/10.1021/jacs.6b08799)). By studying the substituent-dependent regio- and stereoselectivity of three model reactions, the researchers establish a more accurate approach to account for both the electronic and the steric influences.

This study has systematically quantified proximal and remote steric effects in Hammett-type analysis, providing a new strategy to evaluate steric effects in substituted aryl compounds. The rational combination of multiple structural descriptors has created improved and versatile alternatives to Hammett values, greatly expanding the scope of Hammett analysis.

Xin Su, Ph.D.

### ■ NEW WAY TO FIX NITROGEN TO N<sub>2</sub>H<sub>4</sub>

Converting nitrogen gas (N<sub>2</sub>) to ammonia (NH<sub>3</sub>) is a pivotal process both in Nature, providing a way for legumes to enrich the soil, and in industry, supplying an important precursor for fertilizers, explosives, and other products. Although hydrazine (N<sub>2</sub>H<sub>4</sub>) is also a valuable chemical, with uses in fuels and foaming agents and as a precursor to pesticides and pharmaceuticals, reducing N<sub>2</sub> to form this product has proven considerably more difficult due to the endothermic nature of this reaction. No practical and economical route currently exists for directly converting N<sub>2</sub> to N<sub>2</sub>H<sub>4</sub>. Now, Andrew Ashley and co-workers show the power of a simple iron-based catalyst to selectively facilitate reduction of N<sub>2</sub> to N<sub>2</sub>H<sub>4</sub> (DOI: [10.1021/jacs.6b08802](https://doi.org/10.1021/jacs.6b08802)).

The researchers report that the catalyst is highly efficient and has a turnover number comparable to those of the most effective existing molecular catalysts for nitrogen fixation. Moreover, the reaction uses a weaker reductant and takes place under more mildly acidic conditions compared to other N<sub>2</sub> reduction reactions that utilize synthetic iron-based catalysts. The authors suggest that this selective fixation of N<sub>2</sub> to N<sub>2</sub>H<sub>4</sub> could be a viable way to produce hydrazine for industrial uses.

Christen Brownlee

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