Mechanistic Investigations of the Reduction of Nitrogen Containing Compounds by Nitrogenase

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Nitrogenase is the enzyme responsible for biological nitrogen fixation, the conversion of dinitrogen gas into two molecules of ammonia. This is accomplished at a unique 7Fe-9S-Mo-X-homocitrate cofactor referred to as the FeMo-cofactor. Over the past few years, our laboratories have characterized several bound substrates or inhibitors in various intermediate states on the active site of this enzyme, including cyanide and propargyl alcohol. Now, we have shifted our efforts toward compounds with properties more closely related to the physiological substrate dinitrogen. These compounds include dinitrogen as well as more reduced states of dinitrogen, such as hydrazine, a possible intermediate species of dinitrogen reduction.

We present new results obtained through the use of site-specific modifications of residues surrounding the active site that have allowed us to trap hydrazine- and dinitrogen-derived intermediate species bound on the FeMo-cofactor of nitrogenase. These trapped species are amenable to advanced spectroscopic analysis, providing evidence about the nature of the trapped species. We also provide preliminary results from compounds mimicking early reduced states of dinitrogen reduction, as well as kinetic data illustrating how the disruption to the flow of electrons through the enzyme results in the formation of these trapped species.