

Dr. Paul Wagenknecht- Wagenknecht Group Research Projects

Though an inorganic chemist by training, most of my research questions are inspired by problems that have been solved in the exquisite and complex molecular machinery that comprise living systems. Examples of questions that pique my group's interest are: 1) How do the hydrogenase enzymes take kinetically inert hydrogen and utilize it as a reducing agent? 2) In metalloenzyme catalyzed processes, what is the effect of constrained ligand environments around the metal? 3) What affects rates of energy transfer such as occurs in the photosynthetic antenna complex? Thus, my projects fall into two basic categories: catalysis and photochemistry. Our approach to these problems is centered around the chemistry of the transition metals. In general, students in my group experience a broad range of techniques including synthesis, purification, analytical methods (NMR, IR, GC, emission, lifetime...), and kinetic analyses.

Screening of new catalysts for transition metal catalyzed nicotinamide coenzyme regeneration:

The nicotinamide coenzymes, NAD and NADP, belong to a significant class of biomolecules which, in combination with appropriate enzymes, catalyze numerous biochemical oxidations and reductions. These enzymes have attracted widespread interest due to their potential applications in organic synthesis. The nicotinamide coenzymes consumed in stoichiometric quantities in such reductions are very expensive. Thus, practical considerations require recycling the oxidized form of the coenzyme to its reduced, dihydropyridine, counterpart. To be viable a recycling system must generate reduced coenzyme with very high chemical yield and regioselectivity under conditions that are compatible with both the coenzyme and the enzyme. Likewise, a preferred recycling reagent must be inexpensive and not yield byproducts which complicate product purification. Chemical, photochemical, electrochemical and enzymatic recycling methods have been developed but tend to suffer from cumbersome reaction conditions, expensive reagents, and/or unwanted side products. Regenerating NAD(P)H using

dihydrogen (H_2) is preferred because H_2 is the lowest-cost reducing agent and it yields no requisite byproducts. We have recently demonstrated the viability of this direct reduction using water-soluble transition metal complexes as catalysts and have been able to couple the nicotinamide regeneration scheme with an enzymatic reduction of ketones (Figure 1).

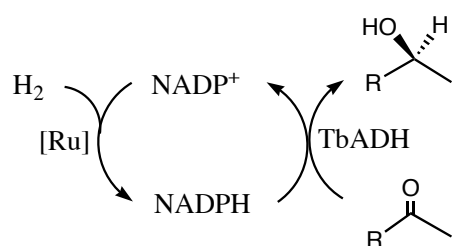


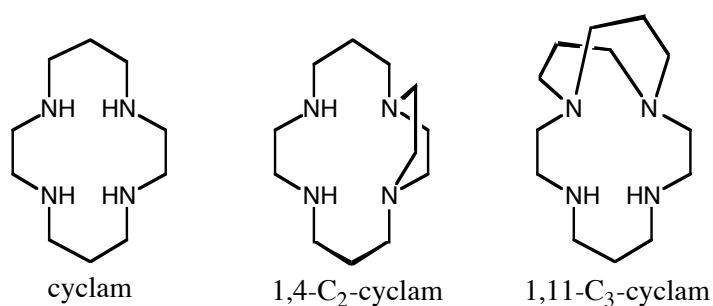
Figure 1. Catalytic cycle

This process, though simple and functional, is slow and suffers from low turnover numbers. In order to achieve the long term goals of developing *efficient* catalysts for this process, methods for screening catalysts and understanding the underlying mechanisms of the individual steps are required. We have developed a simple method of screening water soluble catalysts for their ability to activate dihydrogen and obtain mechanistic information about the hydrogen activation.⁴ We are now beginning the synthesis of new water-soluble ruthenium phosphine complexes and subsequently will be testing their catalytic properties.

Effect of steric constraint on the chemistry and photobehavior of macrocyclic Cr(III) complexes:

Previous photochemical and photophysical studies of Cr(III) complexes of cyclam (Kane-Maguire) have shown that these complexes exhibit relatively long excited state lifetimes and

have been of key importance in understanding general photochemical principles, particularly the relationship between excited state behavior and molecular structure. We wondered what effect geometric constraint would have on the chemistry, photophysics, and photochemistry of these complexes. Therefore, we prepared Cr(III) complexes of two different constrained cyclam ligands, 1,4-C₂-cyclam, and 1,11-C₃-cyclam. The added constraint has a significant effect on the structure, chemistry, and photophysics of these complexes. Particularly, the added steric constraint increases aquation rates by about six orders of magnitude. The decrease in symmetry significantly increases the molar absorptivity and has a marked effect on the photobehavior. The excited state lifetimes of the *trans*-dicyanochromium(III) complexes of the C₃ and C₂ ligands go down by a factor of 10 and 1000, respectively, when compared to the analogous cyclam complex. We are continuing to prepare complexes of these ligands to further our understanding of the effect of steric constraint and for the next project discussed below.



Energy transfer between nearly identical molecules:

Trans-dicyanochromium(III) complexes of the ligands shown above and of other tetraamine and diamine ligands have some very similar excited state properties but are different enough to study energy transfer between them. In collaboration with Professor Kane-Maguire's group we have begun a study of the rates of energy transfer between these complexes as a function of thermodynamic driving force. By understanding how thermodynamics affects energy transfer rates, we can begin to understand thermoneutral energy transfers such as occur in photosynthesis. We have some exciting initial results that suggest that there *may* be something very special about the thermoneutral energy transfers. These results will be put through much scrutiny this summer in a series of energy transfer experiments using pulsed laser lifetime and emission studies.