

Dynamic and Mechanistic Studies of Catalytic Reactions  
Using Photochemical Probes

Leonard D. Spicer

Department of Chemistry  
University of Utah  
Salt Lake City, Utah 84112

Research Scope and Objectives

This research program is designed to study molecular catalysis via photochemical kinetic spectroscopy. The strategy is to use photochemistry to identify mechanistic features in catalytic reactions and to direct catalytic reactions into new and/or normally unfavored reaction channels.

Description of Research Effort

The method used in this research focuses on modifying access to the transition state in a catalytic reaction by selectively energizing the catalyst. Catalysts are characterized by their ability to raise or lower the activation barrier for chemical reactions and this feature also ensures that the effectiveness of the photochemical probe will be manifest in the kinetics of the catalytic reaction. In principle, the light is used to raise the energy of the system before the critical transition state is achieved by depositing energy into the isolated catalyst or the catalyst substrate complex photochemically. When the photon energy is absorbed and utilized directly or degrades to internal modes which participate in the catalytic reaction coordinate, a concurrent marked change in the rate of the catalytic reaction should be observed. If, however, energy is deposited in, or migrates to, coordinates associated with competing reactions, a shift in the favored catalytic path might be expected. Thus, with a suitably intense source of light at the appropriate wavelength, modifications in the catalytic activity or selectivity may occur. The response of the system as a function of wavelength provides additional spectroscopic information in the form of an action spectrum. Spectral features are then correlated with normal mechanisms for the active catalyst and with any modifications in catalyst selectivity observed.

Current initial efforts are focused on the reactions of Wilkinson's catalyst in solution and immobilized on diphenylphosphine modified silica and other inorganic support materials where the anchoring group serves as one of the ligands. This choice was intended to correlate known features of a well-studied homogeneous catalyst with observed spectral results for both homogeneous and heterogeneous systems involving the same or a similar rhodium centered complex. In addition, immobilized metal complexes offer the simplification of a single type of active site in a heterogeneous system and also prevent dimerization or clustering of the rhodium centers. Both photoassistance for olefin hydrogenation and photochemical modification

of the selectivity have been observed in the homogeneous system, and each process appears to be independently initiated over different spectral regions. The photochemical process generates an efficient isomerization catalyst having a half life of several minutes. The action spectra for this catalyst has been determined, and the mechanism postulated for its origin involves ligand rearrangement followed by formation of a fluxional  $\eta^3$ -allyl. The surface bound rhodium complex is currently being prepared in order to explore its action spectra in a similar way. It is anticipated that primary spectral features will not be substantially altered in the immobilized catalyst, thus facilitating a molecular comparison with the homogeneous system.

#### Future Research

The generality of photochemical kinetic spectroscopy will be investigated in a variety of catalytic systems with an emphasis on applications to more complex conventional heterogeneous catalysts. In addition, prospects for photodirecting catalyst selectivity in heterogeneous systems will be explored.