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(NII) - Local Electric Field Effects on Rhodium-Porphyrin and NHC-Gold Catalysts

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Final Report**

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Final Performance Report

Project Title: Local Electric Field Effects on Rhodium-Porphyrin and NHC-Gold Catalysts

Principal Investigator: Matthew W. Kanan

Project Publications:

1. "An Electric Field-Induced Change in the Selectivity of a Metal Oxide-Catalyzed Epoxide Rearrangement" Gorin, C. F.; Beh, E. S.; Kanan, M. W. *J. Am. Chem. Soc.* **2012**, *134*, 186-189.
2. "Interfacial Electric Field Effects on a Carbene Reaction Catalyzed by Rh Porphyrins" Gorin, C. F.; Beh, E. S.; Bui, Q. M.; Dick, G. R.; Kanan, M. W. *J. Am. Chem. Soc.* **2013**, *135*, 11257-11265.
3. "Electrostatic control of regioselectivity via ion pairing in a Au(I)-catalyzed rearrangement" Lau, V. M.; Gorin, C. F.; Kanan, M. W. *Chem. Sci.* **2014**, *5*, 4975-4979.
4. "Catalysis controlled by interfacial electric fields" Kanan, M. W.; Beh, E. S.; Gorin, C. F. US Patent application 14/240723.
5. "Local Electrostatic Effects on the Selectivity of Catalytic Reactions" Gorin, C. F. Stanford University Ph.D. Thesis, July 2014.

Executive Summary:

Controlling the selectivity of catalytic reactions is one of the greatest challenges of synthesizing organic compounds that are essential for health, technology, and defense. Chemists have traditionally addressed this problem using molecular design—i.e. controlling selectivity by changing the molecular structure of the reactants, catalysts or other reaction components. The overall goal of this project was to explore the possibility of using externally applied electric fields to control selectivity. The central idea is that a local electric field will change the potential energy surface for a reaction by creating field-dipole interactions with the reacting species and surrounding solvent molecules. This concept is appealing because all unique ground states and transition states that lead to specific reaction products have unique charge distributions that would respond differently to an electric field. The specific objective of this project was to investigate the effect of local electric fields on catalytic reactions at electrode-electrolyte interfaces. Applying a potential to an electrode in an electrolyte solution places charge density on the electrode that is balanced by the accumulation of electrolyte ions at the interface. The combination of these two charge densities creates large electric fields that on average are oriented normal to the surface. By confining catalytic reactions to this interfacial region, the effect of this electrostatic environment on the selectivity of the reaction can be studied. The major results of this project, including all the data and experimental procedures, are freely available in the publications listed above. The results are briefly summarized below.

To study electrostatic effects on catalytic reactions, a novel reaction vessel called the "parallel plate cell" was designed and fabricated. The cell is composed of two highly doped Si electrodes that sandwich a thin perfluorinated gasket with a small volume for the reaction solution. Each Si electrode is coated with an ultrathin (40–50 Å) layer of an insulating oxide such as Al₂O₃. With an electrolyte solution in between the two oxide-coated Si electrodes, application of a voltage across the electrodes creates electrochemical double layers at the oxide-electrolyte interfaces. The charge density at the interfaces is determined by the interfacial capacitances and the magnitude of the applied voltage. The oxide layers prevent Faradaic processes from occurring within the voltage limits before dielectric breakdown occurs. In the first reactions studied with this cell, the insulating Al₂O₃ layers were themselves used as catalysts for an epoxide rearrangement reaction. The reaction of *cis*-stilbene oxide with an Al₂O₃ surface results in formation of a mixture of aldehyde and ketone products. In the absence of a voltage, the reaction of *cis*-stilbene oxide with an Al₂O₃ layer in the parallel plate cell in an organic electrolyte solution gave the same ratio as was obtained with Al₂O₃ powder in a conventional flask reaction. The

aldehyde:ketone product ratio increased upon application of a voltage to the parallel plate cell. The magnitude of the change in the ratio increased as the voltage was increased, up to a 63-fold change at the maximum voltage that could be applied before dielectric breakdown. Various control experiments indicated that the change in product ratio depended on the charge density at the Al₂O₃-electrolyte interfaces, which is consistent with an electrostatic effect on the reaction. Interestingly, the aldehyde:ketone ratio increased for both a positive and negative voltage drop at the Al₂O₃-electrolyte interface. This result suggests that there may be significant dipole alignment of intermediates in the interfacial field or that the effect on selectivity arises from perturbation of the solvation properties in the interfacial region. Full details of this study are available in the publication (*J. Am. Chem. Soc.* **2012**, *134*, 186-189).

The next question addressed was whether an interfacial electric field could affect the selectivity of a reaction catalyzed by a molecular catalyst. An intramolecular carbene reaction catalyzed by a Rh porphyrin was selected as a model reaction for this study. A diazoketone substrate was designed to react with Rh porphyrin catalysts via a Rh metallocarbenoid intermediate to form a mixture of intramolecular cyclopropanation and C-H insertion products. Under traditional homogeneous reaction conditions, the reaction favors cyclopropanation over insertion by a ratio of approximately 10:1. When the Rh porphyrin was localized to the oxide-electrolyte interface in the parallel plate cell, application of a voltage to the cell changed the product ratio in a direction that depended on the oxide surface chemistry. The Rh porphyrin was localized to the interface by covalent attachment through phosphonate linkages or spontaneous physisorption under the experimental conditions. With an Al₂O₃ oxide or any insulating oxide coated with an alkyl phosphonate monolayer, application of a voltage caused the cyclopropanation:insertion product ratio to decrease. The magnitude of the decrease was dependent on the charge density at the interface and the maximum effect observed was to change the ratio to 1:2 in favor of the insertion product at the most highly charged interface. This effect was attributed to an electrostatic perturbation of the potential energy surface for the reaction. With a TiO₂ oxide coating, however, increasing the charge density at the interface caused the cyclopropanation:insertion product to increase. At the highest charge density that could be achieved before dielectric breakdown, the ratio was >100:1. It was determined through a variety of additional experiments that a charge density-induced chemical interaction between the TiO₂ surface and the Rh porphyrin catalyst was responsible for the selectivity change. Full details of this study are available in the publication (*J. Am. Chem. Soc.* **2013**, *135*, 11257-11265).

The experiments in the parallel plate cell showed that polarized electrode-electrolyte interfaces could significantly change the selectivity of catalytic reactions. Elucidating the specific electrostatic or other interactions that are responsible for the selectivity changes is challenging because the interfacial environment is highly complex and the energetic differences associated with the observed selectivity changes are small. To study electrostatic effects in a simpler context, we studied the effects of ion pairing on the selectivity of an intramolecular rearrangement catalyzed by cationic Au(I) complexes. The reaction selected was the rearrangement of aryl alkynyl sulfoxides to form dihydrobenzothiepinones via a putative Au metallocarbenoid intermediate. With aryl alkynyl sulfoxides that are substituted at the 3 position, the reaction yields two regioisomeric products. The regioselectivity is very difficult to control because it is not very sensitive to the ligand on the Au(I) complex. The reaction was performed with a variety of cationic Au(I) catalysts with different counterions in solvents that spanned a range of dielectric constants (ϵ). Using diffusion NMR techniques, it was determined that the Au(I) catalysts are tightly ion paired to their counterions in solvents with $\epsilon < 5$ and essentially non-paired in solvents with $\epsilon > 6$. For solvents in which there is no ion pairing, the regioselectivity of the reaction (i.e. the product ratio) was insensitive to ϵ . For solvents in with $\epsilon < 5$, however, the ratio changed monotonically as ϵ was decreased. The magnitude of the selectivity change depended on the

identity of the substituent at the 3 position. The largest change (6.3-fold from reaction in solvents with $\epsilon > 6$ to reaction in toluene, for which $\epsilon = 2.2$) was obtained with a CF_3 substituent, and, at the other extreme, almost no change was observed with a CH_3 substituent. To understand this disparity, DFT calculations were performed for the two putative product-determining transition states for each substrate. It was observed that the magnitude of the change in the product ratio in going from high- ϵ to low- ϵ solvent was correlated with the magnitude of the difference in dipole moments between the two competing transition states. In all cases, ion pairing favored the product resulting from the more polar transition state. It was concluded that ion pairing electrostatically differentiates the competing transition states by a field-dipole effect. Full details of this study can be found in the publication (*Chem. Sci.* **2014**, *5*, 4975–4979).

In summary, the project has demonstrated the feasibility of two methods for exploiting electrostatic effects to change the selectivity of reactions: using electrically polarized solid-liquid interfaces and using ion pairs in low- ϵ solvents. Ongoing work is exploring the use of electrostatic effects derived from ion pairing to control the selectivity of synthetically important group transfer reactions and the use of ferroelectric materials as dispersible, permanently polarized interfaces that substitute for electrode-electrolyte interfaces.

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Matthew W. Kanan

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The AFOSR Program Manager currently assigned to the award

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Abstract

Controlling the selectivity of catalytic reactions is one of the greatest challenges of synthesizing organic compounds that are essential for health, technology, and defense. The purpose of this project was to investigate the use of externally applied electric fields to control the selectivity of reactions in a way that is complementary to conventional methods. Using a custom reaction vessel, it was shown that the selectivity of reactions that are confined to an insulating electrode–electrolyte interface could be altered by the application of a voltage across the interface. The magnitude of the selectivity changes depended on the charge density that accumulated at the interface, which was controlled by the voltage and the interfacial capacitance. The selectivity of an Al₂O₃-catalyzed epoxide rearrangement reaction was changed by up to a factor of 63 at the highest charge density that could be achieved before dielectric breakdown. The selectivity of a Rh porphyrin–catalyzed intramolecular carbene reaction could be altered by a total of a factor of 200 depending on the charge density and the surface chemistry of the electrode–electrolyte interface. It was proposed that the charge density affects the reaction outcome through local field–dipole interactions with the reacting species

themselves and/or the surrounding solvent molecules. In a separate set of experiments, it was shown that field–dipole interactions that arise in tight ion pairs could be exploited to control selectivity. The counterion to a reactive complex in a tight ion pair preferentially stabilizes transition states with the largest dipole moments. These effects were demonstrated for a alkynyl sulfoxide rearrangement reaction catalyzed by cationic Au(I) complexes.

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