

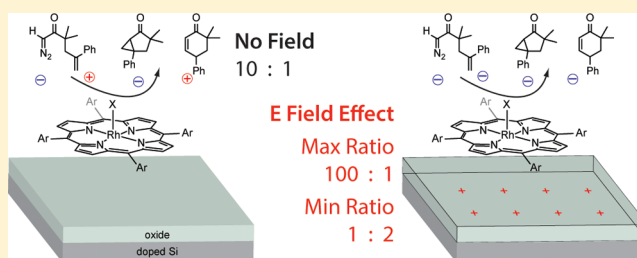
Interfacial Electric Field Effects on a Carbene Reaction Catalyzed by Rh Porphyrins

Craig F. Gorin, Eugene S. Beh, Quan M. Bui, Graham R. Dick, and Matthew W. Kanan*

Department of Chemistry, Stanford University, Stanford, California 94305, United States

S Supporting Information

ABSTRACT: An intramolecular reaction catalyzed by Rh porphyrins was studied in the presence of interfacial electric fields. 1-Diazo-3,3-dimethyl-5-phenylhex-5-en-2-one (**2**) reacts with Rh porphyrins via a putative carbenoid intermediate to form cyclopropanation product 3,3-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one (**3**) and insertion product 3,3-dimethyl-2,3-dihydro-[1,1'-biphenyl]-4(1*H*)-one (**4**). To study this reaction in the presence of an interfacial electric field, Si electrodes coated with thin films of insulating dielectric layers were used as the opposing walls of a reaction vessel, and Rh porphyrin catalysts were localized to the dielectric–electrolyte interface. The charge density was varied at the interface by changing the voltage across the two electrodes. The product ratio was analyzed as a function of the applied voltage and the surface chemistry of the dielectric layer. In the absence of an applied voltage, the ratio of **3**:**4** was approximately 10:1. With a TiO₂ surface, application of a voltage induced a Rh porphyrin–TiO₂ interaction that resulted in an increase in the **3**:**4** ratio to a maximum in which **4** was nearly completely suppressed (>100:1). With an Al₂O₃ surface or an alkylphosphonate-coated surface, the voltage caused a decrease in the **3**:**4** ratio, with a maximum effect of lowering the ratio to 1:2. The voltage-induced decrease in the **3**:**4** ratio in the absence of TiO₂ was consistent with a field–dipole effect that changed the difference in activation energies for the product-determining step to favor product **4**. Effects were observed for porphyrin catalysts localized to the electrode–electrolyte interface either through covalent attachment or surface adsorption, enabling the selectivity to be controlled with unfunctionalized Rh porphyrins. The magnitude of the selectivity change was limited by the maximum interfacial charge density that could be attained before dielectric breakdown.



■ INTRODUCTION

The development of a selective catalyst for a chemical reaction requires control over the relative energies of competing activation barriers. This challenge has typically been addressed from a structure–activity perspective. Specifically, chemists have focused on identifying the steric and electronic properties of the catalyst that result in the lowest barriers for a desired pathway. A complementary strategy is to change the local environment in which a reaction takes place. While researchers commonly screen different solvents to optimize a reaction, methods to alter the reaction environment independently of changing the solvent are not generally available. In particular, there has been very little effort to control the local electrostatic environment in the vicinity of an active catalyst. A strong local electric field could in principle change the outcome of a reaction through field–dipole interactions with the catalyst, reactants, or solvent molecules surrounding them. If local electric fields could be applied by adjusting an external parameter, these effects could be widely exploited to control selectivity.

The concept of electric field control has been explored computationally. Density functional theory studies have concluded that constant electric fields on the order of 1–10 V/nm perturb activation barriers for gas-phase reactions by up

to several kcal/mol, an amount sufficient to change the selectivity by orders of magnitude at room temperature.^{1–3} In practice, applying a large electric field to a reaction is challenging because large voltages applied over macroscopic distances result in dielectric breakdown. Field strengths on the order of 0.01–0.1 V/nm can be applied to thin (~μm) frozen solutions before breakdown.⁴ These fields have been shown to affect the rates of electron transfer reactions for which there are large changes in dipole moment.^{5,6}

Large electric fields can be applied over molecular length scales by controlling the placement of ionic and polar molecules. This concept has been extensively studied in biological systems. A combination of experimental and computational studies has indicated that oriented electric fields on the order of multiple V/nm are created in enzyme active sites by the placement of polar residues.^{7–9} These fields may substantially decrease activation barriers in enzymatic catalysis.^{10,11} In an example from heterogeneous catalysis, local electric fields of 1–10 V/nm that arise from proximal cations in zeolite cavities have been exploited to accelerate photocatalytic hydrocarbon oxidations.^{12,13} To exploit field–dipole interac-

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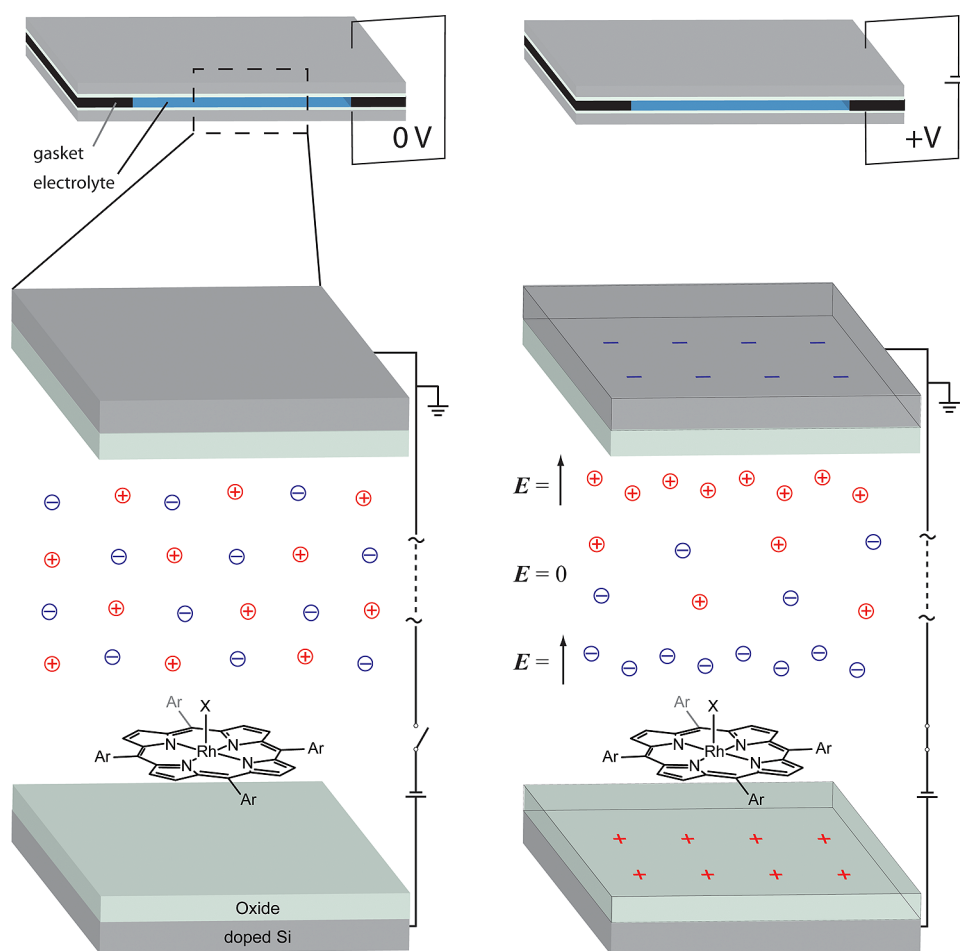


Figure 1. Parallel plate cell. Cross-sectional illustration of the cell (top) and expanded illustration of the metal oxide–electrolyte interfaces with localized Rh porphyrin catalyst (bottom) at 0 V (left) and positive voltage (right). Significant V-dependent electric fields are present only at the interfaces.

tions in the most general manner, however, an easy way of applying large local electric fields to reaction centers via an externally adjustable parameter is needed. One possibility is to exploit the electric fields that are present in the double layer region at the interface between a polarized electrode and an electrolyte solution.¹⁴ These interfacial fields arise from the combination of surface charge density on the polarized electrode and accumulation of oppositely charged ions from the electrolyte solution. The polarity and magnitude of these interfacial fields are controlled by the voltage applied to the electrode. By attaching molecules to electrode surfaces, previous studies have shown that interfacial electric fields affect electron transfer rates to enzymes^{15,16} and the position of a tautomerization equilibrium of a synthetic molecule.¹⁷

Exploiting interfacial electric fields to control selectivity in catalysis requires confining catalytic reactions to polarized interfaces and suppressing undesired electron transfer processes. We recently developed a reaction vessel, the “parallel plate cell”, that enables thin-film metal oxide catalysts to be subjected to interfacial electric fields. Using this cell, we showed that the selectivity of an Al_2O_3 -catalyzed epoxide rearrangement changed by up to a factor of 63 as the charge density at the Al_2O_3 –solution interface was increased.¹⁸ The selectivity changes were consistent with an electrostatic effect on the competing activation barriers. We hypothesized that a molecular catalyst could also be subjected to interfacial electric

fields in the parallel plate cell by localizing the catalyst to the metal oxide–electrolyte interface. The design of a cell suitable for experiments with a molecular catalyst is shown in Figure 1, using a Rh porphyrin as an example. Briefly, the parallel plate cell consists of two heavily doped Si electrodes and a thin perfluorinated gasket. Each electrode is coated on its polished side with a thin insulating dielectric. Molecular catalysts are localized to the interface between the dielectric and the electrolyte solution through covalent attachment or surface adsorption. In an assembled cell, the electrodes are pressed against opposite sides of the gasket, and an electrolyte solution containing the substrate for a reaction occupies the volume between the two electrodes. Application of a voltage between the two electrodes generates electrochemical double layers that give rise to interfacial electric fields at each electrode–electrolyte interface.

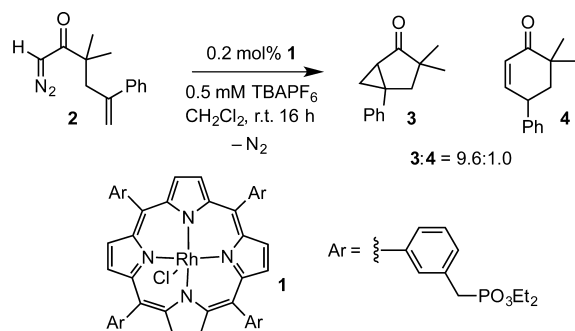
Here, we describe parallel plate cell reactions to study electrostatic effects on an intramolecular carbene reaction catalyzed by Rh porphyrins. Our results demonstrate that the selectivity of a molecular catalyst can be changed by subjecting the catalyst to an interfacial electric field.

RESULTS

To covalently bind a molecular catalyst to the dielectric–electrolyte interface in the parallel plate cell, we prepared Rh tetraarylporphyrin **1**, which has four phosphonate esters

(Scheme 1).^{19,20} Highly doped Si wafers coated with 45 Å of atomic layer deposition (ALD)-deposited Al_2O_3 (" $\text{Al}_2\text{O}_3/\text{Si}$ ")

Scheme 1



electrodes") were prepared as described previously.¹⁸ **1** was attached to the Al_2O_3 surface via phosphonate– Al_2O_3 linkages by using a variant of available procedures for attaching alkane phosphonate monolayers to Al_2O_3 (see the Supporting Information). The electrode was subsequently sonicated in CH_3OH and THF and soaked in CH_2Cl_2 to remove multilayers of **1**. X-ray photoelectron spectroscopy (XPS) of the resulting **1**-functionalized electrode (" $\text{1}/\text{Al}_2\text{O}_3/\text{Si}$ ", Figure 2) exhibited the expected Rh, N, and P peaks for **1** in the appropriate ratios (Figure S2). The Rh:Al ratio was 1:73, which is consistent with an approximate monolayer coverage. XPS spectra of an analogous porphyrin-functionalized $\text{Al}_2\text{O}_3/\text{Si}$ electrode before and after subjecting it to conditions for a parallel plate cell reaction (see below) showed no appreciable decrease in surface coverage (Figures S6, S7), indicating stability of the phosphonate– Al_2O_3 linkage.

The voltage-dependent charge densities in the parallel plate cell were measured by using double-step chronocoulometry.

Cells were assembled with one $\text{1}/\text{Al}_2\text{O}_3/\text{Si}$ electrode, one bare $\text{Al}_2\text{O}_3/\text{Si}$ electrode, and 0.5 mM tetrabutylammonium hexafluorophosphate (TBAPF_6) in CH_2Cl_2 between the two electrodes. The charge density increased in an approximately linear manner up to $2.6 \mu\text{C}/\text{cm}^2$ at 5 V (Figure 3), beyond which dielectric breakdown occurred. Similar charge densities were observed in parallel plate cells with two bare $\text{Al}_2\text{O}_3/\text{Si}$ electrodes.

The reaction chosen for electric field effect studies was a Rh-catalyzed intramolecular carbene reaction using a diazoketone as a carbene precursor (Scheme 1).^{21,22} Carbene reactions are powerful methods for forming C–C bonds, but controlling their chemoselectivity is often very challenging.^{23,24} Diazoketone **2** was selected as a model substrate because it reacts under mild conditions at low catalyst loadings and forms predominantly two products. For comparison to subsequent reactions in the parallel plate cell, the reaction was first performed in a vial under standard homogeneous conditions. In a CH_2Cl_2 solution containing 1 mM diazoketone **2** and 0.5 mM tetrabutylammonium hexafluorophosphate (TBAPF_6), 0.2 mol % **1** catalyzed the reaction of **2** to form bicyclohexanone **3** and cyclohexenone **4** in a 9.6:1.0 ratio. A similar ratio was observed in the absence of electrolyte.

A series of parallel plate cell reactions were performed with cells comprised of one $\text{1}/\text{Al}_2\text{O}_3/\text{Si}$ electrode, one bare $\text{Al}_2\text{O}_3/\text{Si}$ electrode, and a CH_2Cl_2 solution containing 1 mM diazoketone **2** and 0.5 mM TBAPF_6 (Figure 2). After the parallel plate cell was assembled, a constant voltage was applied between the electrodes for 19 h. The cell was subsequently disassembled, and the product mixture was analyzed by high performance liquid chromatography (HPLC). Product ratios were analyzed for voltages ranging from 0 to ± 5 V (Figure 2). Small leakage currents of 0–8 nA/ cm^2 were observed for this voltage range. Beyond 5 V, leakage currents were much larger and increased over time, indicating dielectric breakdown. At sub-breakdown

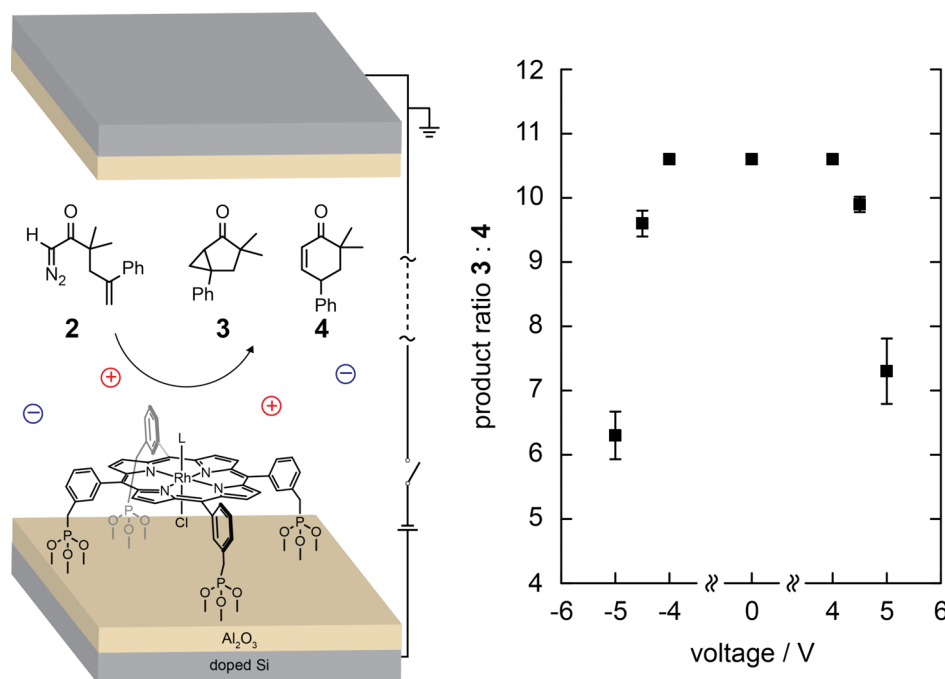


Figure 2. Schematic of the parallel plate cell reaction with attached **1** (left). Product ratios as a function of voltage for parallel plate cell reactions with one $\text{1}/\text{Al}_2\text{O}_3/\text{Si}$ electrode, one bare $\text{Al}_2\text{O}_3/\text{Si}$ electrode, and a CH_2Cl_2 solution containing 1 mM diazoketone **2** and 0.5 mM TBAPF_6 (right).

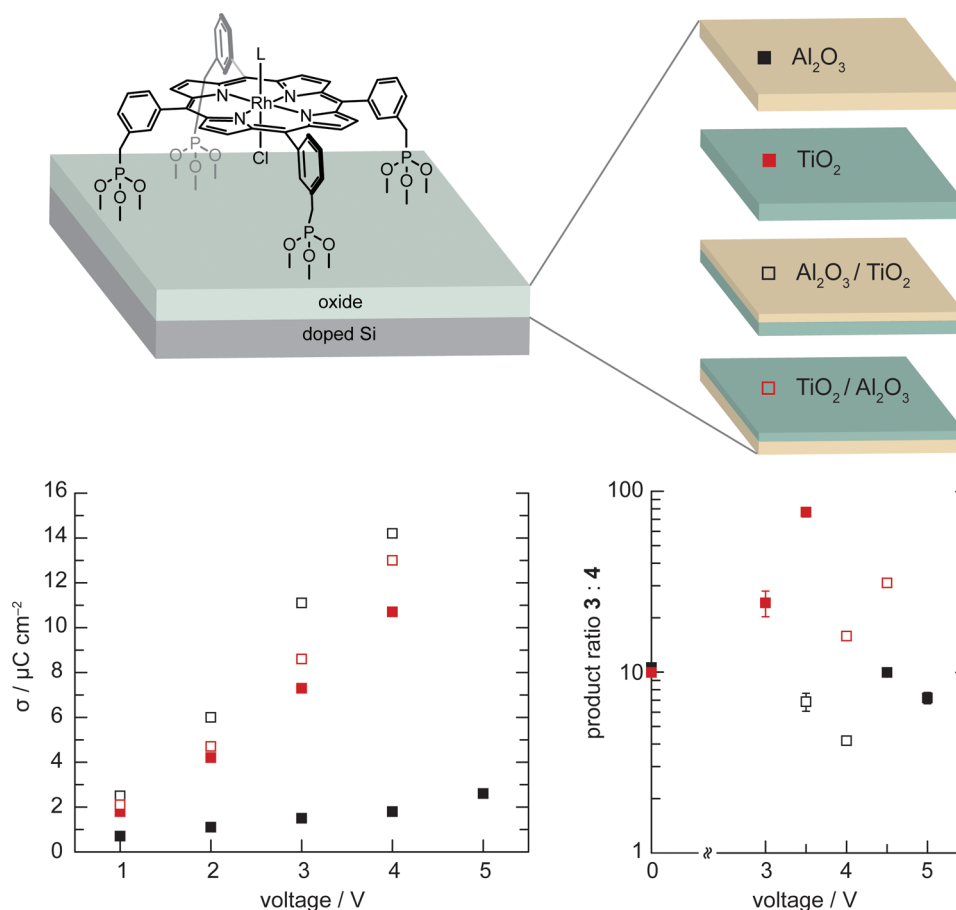


Figure 3. Schematic of electrodes used in parallel plate cell reactions with attached **1** including $1/\text{Al}_2\text{O}_3/\text{Si}$ (■), $1/\text{TiO}_2/\text{Si}$ (red ■), $1/\text{Al}_2\text{O}_3/\text{TiO}_2/\text{Si}$ (□), and $1/\text{TiO}_2/\text{Al}_2\text{O}_3/\text{Si}$ (red □) (top). Chronocoulometric measurement of charge density (σ) at selected voltages in the parallel plate cell with 0.5 mM TBAPF₆ in CH_2Cl_2 on the various electrodes (bottom left). Product ratios as a function of voltage for parallel plate cell reactions with one electrode with attached **1**, one bare electrode, and a CH_2Cl_2 solution containing 1 mM diazoketone **2** and 0.5 mM TBAPF₆ (bottom right).

voltages, typical conversions after 19 h were 20–30%, and **3** and **4** were the only significant products observed by HPLC. At 0 V, the reaction of **2** formed **3** and **4** in a 10.6:1.0 ratio, similar to the ratio obtained for the reaction performed in a vial with homogeneous **1**. At $|V| < 4.5$ V, no effect on the product ratio was evident. At +4.5 V, however, the 3:4 ratio decreased slightly to 9.8:1.0. At +5 V, the 3:4 ratio decreased further to 7.2:1.0, representing a ~ 1.5 -fold change relative to the reaction at 0 V. Similar results were observed at -4.5 and -5 V, where the 3:4 ratios were 9.5:1.0 and 6.3:1.0, respectively. Similarity between selectivity changes at positive and negative voltages was also observed in our previous study of an Al_2O_3 -catalyzed epoxide rearrangement reaction in the parallel plate cell.¹⁸

Several experiments were performed to assess contributions of nonelectrostatic factors to the voltage-dependent selectivity changes in the parallel plate cell (see the Supporting Information). Parallel plate cell reactions performed with two bare $\text{Al}_2\text{O}_3/\text{Si}$ electrodes in the absence of **1** showed no conversion, even at +5 V. This result indicates that the Al_2O_3 surface and any electrolytic product generated by the small leakage currents are incapable of catalyzing the formation of a carbene from diazoketone **2**. Parallel plate cell reactions performed at +5 V with **1** as described above exhibited product ratios after 4 h similar to those seen after 19 h, indicating that the leakage current does not result in the formation of an electrolytic product that accumulates in the solution and alters the selectivity of the catalyst. Additionally, when electrodes

functionalized with **1** that had previously been used in parallel plate cells at +5 V were reused at 0 V with fresh solutions of **2** in the electrolyte, the product ratios for these experiments were the same as those for a previously unused electrode at 0 V. This result indicates that the application of a voltage does not lead to an irreversible redox reaction of the catalyst to generate a catalytically active species that exhibits different selectivity.

In addition to the applied voltage, the charge density that an electrode-localized catalyst experiences in the parallel plate cell depends on the electrical and chemical properties of the insulating dielectric layer. In an attempt to increase the magnitude of voltage-dependent selectivity changes, we explored alternatives to Al_2O_3 . ALD-deposited titania (TiO_2) has a higher dielectric constant than ALD-deposited Al_2O_3 (32 vs 7).²⁵ We prepared Si wafers coated with 50 Å of ALD-deposited TiO_2 . Double-step chronocoulometry with parallel plate cells assembled from these electrodes (“ TiO_2/Si ”) exhibited charge densities that increased linearly up to 10.7 $\mu\text{C}/\text{cm}^2$ at ± 4 V, beyond which breakdown occurred (Figure 3). These results suggest that larger interfacial charge densities are available within the breakdown window for TiO_2/Si electrodes as compared to $\text{Al}_2\text{O}_3/\text{Si}$ electrodes, although the extent of oxide charging in the parallel plate cell may differ for these two interfaces (see Discussion).

1 was attached to a TiO_2/Si electrode by using the same deposition method as for attachment to $\text{Al}_2\text{O}_3/\text{Si}$, and the functionalized electrode (“**1**/ TiO_2/Si ”) was characterized by

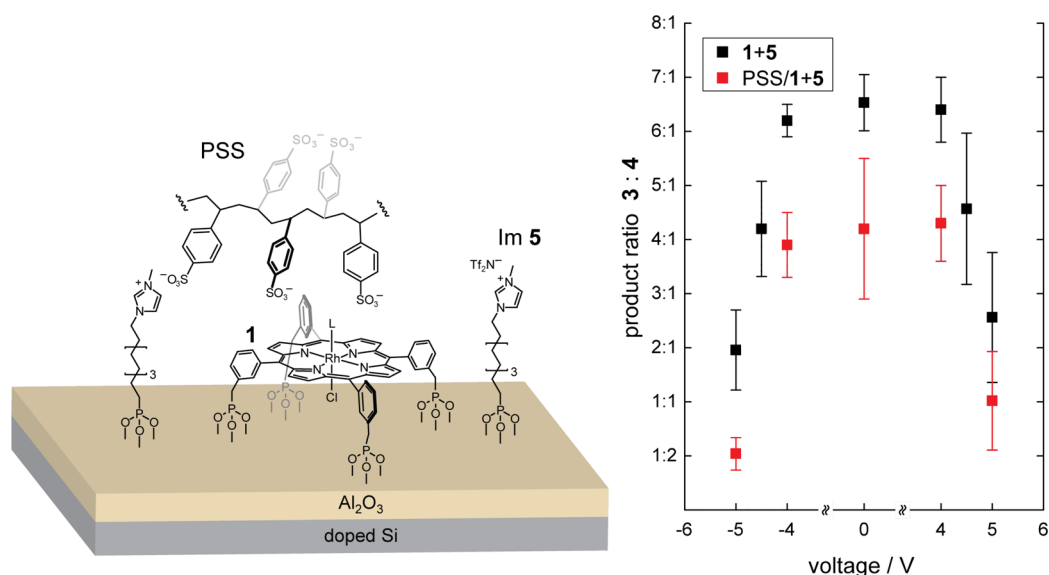


Figure 4. Schematic of the 1+5/Al₂O₃/Si and PSS/1+5/Al₂O₃/Si electrodes (left). Product ratios as a function of voltage for parallel plate cell reactions with one electrode with attached 1+5 (■) or attached PSS/1+5 (red ■), one bare electrode, and a CH₂Cl₂ solution containing 1 mM diazoketone 2 and 0.5 mM TBAPF₆ (right).

XPS. Parallel plate cell reactions were performed in cells comprised of one 1/TiO₂/Si electrode and one bare TiO₂/Si electrode under the conditions described above at voltages ranging from 0 to ± 4 V. The product ratio again exhibited dependence on applied voltage, but in the direction opposite to that of the Al₂O₃-coated electrodes (Figure 3). At 0 V, the rearrangement of 2 proceeded to form 3 and 4 in a 10.1:1.0 ratio, similar to the ratio observed with 1/Al₂O₃/Si. At $|V| < 3$ V, no effect on the product ratio was evident. At +3.0 and +3.5 V, the 3:4 ratio increased to 24:1.0 and 75:1.0, respectively. At +4 V, only product 3 was detectable by HPLC, representing a 3:4 ratio $>100:1$ and at least a 10-fold change relative to the reaction at 0 V. Similar selectivity changes in favor of product 3 were observed at negative voltages.

The disparity in the voltage-dependent selectivity changes for 1 on Al₂O₃ as compared to TiO₂ suggests that voltage-dependent oxide–Rh porphyrin interactions may be operative in one or both cases. To assess this possibility, we prepared electrodes coated with oxide stacks.²⁶ Si wafers were coated with 10 Å of TiO₂ atop 40 Å of Al₂O₃ ("TiO₂/Al₂O₃/Si") or 10 Å of Al₂O₃ atop 40 Å of TiO₂ ("Al₂O₃/TiO₂/Si"). The electrodes were functionalized with 1 and characterized as described above. Double step chronocoulometry measurements of parallel plate cells with oxide stacks exhibited larger charge densities than either oxide alone, increasing up to 14 $\mu\text{C}/\text{cm}^2$ for Al₂O₃/TiO₂/Si and 13 $\mu\text{C}/\text{cm}^2$ for TiO₂/Al₂O₃/Si (Figure 3). A set of parallel plate cell reactions were performed with cells comprised of a 1/Al₂O₃/TiO₂/Si electrode and an Al₂O₃/TiO₂/Si electrode under the same conditions described above. The observed 3:4 ratio at 0 V matched the ratio seen previously. Application of a voltage induced a change in the selectivity in the same direction as seen with a 1/Al₂O₃/Si electrode, but the magnitude of the change was larger and required a smaller voltage. The 3:4 ratio reached 4.1:1.0 at +4 V, the maximum voltage before breakdown. A second set of parallel plate cell reactions were performed with cells comprised of a 1/TiO₂/Al₂O₃/Si electrode and a bare TiO₂/Al₂O₃/Si electrode under otherwise identical conditions. The observed 3:4 ratio at 0 V was again the same. Application of a voltage

induced a change in selectivity in the same direction as seen with a 1/TiO₂/Si electrode, but the magnitude of the change was smaller and required a larger voltage. The 3:4 ratio reached 35:1.0 at +4.5 V, the maximum voltage before breakdown. These results indicate the direction of the voltage-dependent selectivity change is dependent on the oxide surface, while the magnitude depends on the electrical properties of the dielectric layer.

We hypothesized that greater voltage-dependent charge densities at the dielectric–electrolyte interface could be obtained by using electrodes decorated with ionic functionality. To this end, we codeposited 1 and phosphonate-linked methylimidazolium bis(trifluoromethanesulfonyl)imide 5 on Al₂O₃/Si electrodes to form "1+5/Al₂O₃/Si" electrodes (Figure 4). XPS indicated approximately a 1:3 ratio of 1:5 on the surfaces of these electrodes. Parallel plate cell reactions were performed with cells comprised of a 1+5/Al₂O₃/Si electrode and a bare Al₂O₃/Si electrode under the conditions described above. At 0 V, the observed 3:4 ratio was 6.6:1.0, significantly lower than the ratio observed in the absence of 5. This result is consistent with a perturbed electrostatic environment for 1 in the vicinity of codeposited 5. Application of a voltage caused a change in selectivity in the same direction as for electrodes without 5 but with larger magnitudes. At +4.5 V the ratio was 4.6:1.0, and at +5 V the ratio was 2.6:1.0, representing 1.4- and 2.5-fold changes in selectivity, respectively. Very similar results were observed at -4.5 and -5 V. In control experiments, adding 5 to a reaction in a vial catalyzed by 1 had no effect on the 3:4 ratio.

To further increase the ionic strength of the interfacial region, we added a polystyrenesulfonate layer to 1+5/Al₂O₃/Si electrodes to form "PSS/1+5/Al₂O₃/Si" electrodes. XPS indicated that the original triflimide counterions to the methylimidazolium groups on 1+5/Al₂O₃/Si electrodes were exchanged with sulfonate from PSS on PSS/1+5/Al₂O₃/Si electrodes (Figure S14). Parallel plate cell reactions were performed in cells comprised of a PSS/1+5/Al₂O₃/Si electrode and a Al₂O₃/Si electrode under the conditions described above. Although the addition of the PSS layer decreased the

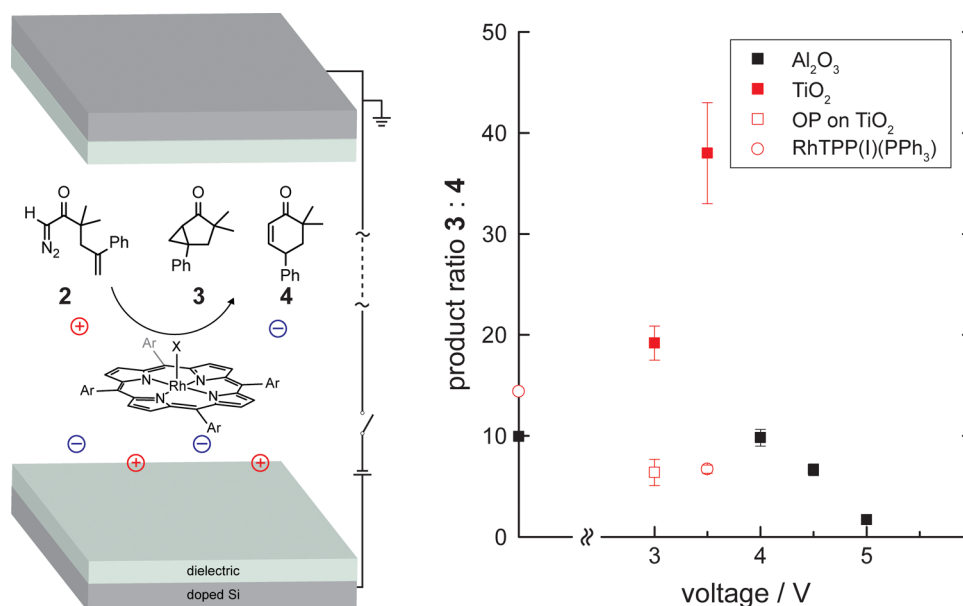


Figure 5. Schematic of the parallel plate cell reaction with unattached Rh porphyrin (left). Product ratios as a function of voltage for parallel plate cell reactions with two Al₂O₃/Si electrodes (■) or two TiO₂/Si electrodes (red ■) or two octylphosphonate/TiO₂/Si electrodes (red □) and a CH₂Cl₂ solution containing 2 μ M **1**, 1 mM diazoketone **2**, and 0.5 mM TBAPF₆ (right). Also shown is the product ratio as a function of voltage for parallel plate cell reactions with two TiO₂/Si electrodes and a CH₂Cl₂ solution containing 2 μ M RhTPP(I)(PPh₃), 1 mM diazoketone **2**, and 0.5 mM TBAPF₆ (red ○).

conversion of **2**, the voltage-dependent selectivity changes were considerably larger (Figure 4). At 0 V, the 3:4 ratio was 4.4:1.0, a further decrease from the ratio observed with a **1**+5/Al₂O₃/Si electrode at 0 V. At -5 V, the ratio was 1.0:1.9, corresponding to an 8-fold change in selectivity.

Chemically attaching a catalyst to the oxide surface enforces its localization to the dielectric–electrolyte interface in the parallel plate cell. In principle, however, an unattached catalyst could spontaneously localize to the interface via adsorption on the surface or by accumulating in the higher ionic strength solution in the interfacial region. To assess whether voltage-dependent selectivity changes could be achieved with unattached catalysts, we performed parallel plate cell reactions with bare Al₂O₃/Si electrodes and 2 μ M **1** added to the solution. This concentration corresponds to 50 pmol of **1** per cm² of electrode surface, an amount sufficient for approximate monolayer coverage. Typical conversions after 19 h under these conditions ranged from 30–50%. At 0 V, the 3:4 ratio was 9.5:1.0, similar to the reaction performed in a vial at higher catalyst loading. At +4.5 and +5 V, the ratio decreased to 6.6:1.0 and 1.6:1.0, corresponding to 1.4- and 5-fold changes in selectivity (Figure 5). Similar results were observed with Rh tetraphenylporphyrin iodide (RhTPP(I)) used as the catalyst instead of **1**. These results suggest that dissolved Rh porphyrins are able to localize to the electrode–electrolyte interface,²⁷ where they experience the interfacial electrostatic environment when a voltage is applied. If this model is correct, the voltage-dependent selectivity changes should be suppressed in the presence of a molecule that can compete with a Rh porphyrin for binding to the surface. To test for such an effect, we repeated the experiments with 2 μ M **1** and 50 μ M of free base tetraphenylporphyrin (H₂TPP) added to the solution. At +5 V under these conditions, the 3:4 ratio was 8.9:1.0, very close to the ratio observed at 0 V.

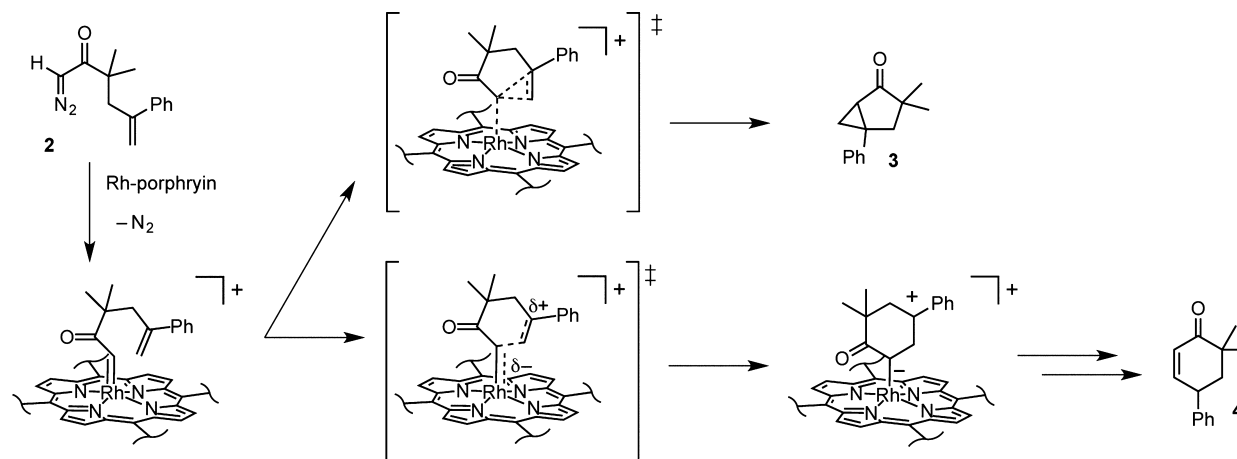
The use of an unattached catalyst in parallel plate cell reactions enabled experiments that probed the effect of the

oxide surface chemistry. The effect of blocking the oxide surface with an alkylphosphonate layer was examined. Octylphosphonate/Al₂O₃/Si electrodes were prepared by soaking Al₂O₃/Si electrodes in solutions of octylphosphonic acid. Reactions were performed under the conditions described above with 2 μ M unattached **1** in parallel plate cells comprised of two octylphosphonate/Al₂O₃/Si electrodes. Similar voltage-dependent selectivity changes were observed in these reactions as compared to the reactions with bare Al₂O₃/Si electrodes, although the magnitudes were somewhat smaller (see the Supporting Information). The results suggest that catalyst localization does not require a bare oxide surface.

A complementary set of parallel plate cell reactions was performed with unattached **1** and either bare TiO₂/Si or octylphosphonate/TiO₂/Si electrodes. With bare TiO₂/Si electrodes and unattached **1**, similar voltage-dependent increases in the 3:4 ratio were observed as compared to experiments with **1** attached to TiO₂. With octylphosphonate/TiO₂/Si electrodes and unattached **1**, however, application of a voltage decreased the 3:4 ratio, mimicking the changes observed when Al₂O₃/Si electrodes were used (Figure 5). Divergent results were also obtained for parallel plate cell reactions performed with bare TiO₂/Si electrodes and either RhTPP(I) or RhTPP(I)(PPh₃) as the catalyst. With RhTPP(I), the 3:4 ratio increased at +3 and +3.5 V, as seen when unattached **1** was used as the catalyst. However, with RhTPP(I)(PPh₃), the 3:4 ratio decreased at +3 and +3.5 V, as seen with unattached **1** when octylphosphonate/TiO₂/Si electrodes were used.

Additional experiments were performed to assess other potential effects on the product ratio. Parallel plate cell reactions performed with any two modified Si electrodes in the absence of **1** showed no conversion, even at high applied potential. Parallel plate cell reactions with bare TiO₂/Si electrodes with 2 μ M **1** added to the electrolyte were run at +3.5 V until the current stabilized (5 min), then shorted for the

Scheme 2



remainder of the reaction. The product distribution indicated no change from 0 V, indicating the proposed 1–TiO₂ interaction requires the constant application of voltage. To test the effect of ionic strength of the solution on selectivity, reactions were performed in a vial with 1 mM diazoketone **2** and 2 μ M **1** in either 50 mM or saturated TBAPF₆ in CH₂Cl₂. In both cases, 3:4 ratios were obtained that were similar to those for reactions performed in 0.5 mM TBAPF₆. Parallel plate cell reactions performed with tetraoctylammonium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (TOABAr^F₄) as the electrolyte also demonstrated a change in the product ratio at +5 V to 4.7:1, indicating TBAPF₆ is not required for the observed effects. Finally, mass spectrometry analysis of the reaction solution after use in a parallel plate cell with bare Al₂O₃/Si electrodes and 2 μ M RhTPP(I) at 0 and +5 V indicated no difference in the major catalyst ions present (Figure S15).

DISCUSSION

A Rh porphyrin–catalyzed reaction of diazoketone **2** intrinsically favors cyclopropanation product **3** over insertion product **4** by an approximate ratio of 10:1. The parallel plate cell experiments demonstrate that when the reaction occurs at the interface between a dielectric layer and an electrolyte solution, the selectivity changes when the interface is charged by the application of a voltage. The direction of the voltage-induced selectivity change depends on the nature of the dielectric surface. The use of a dielectric with a TiO₂ surface results in an increase in the 3:4 ratio upon application of a voltage, while the use of a dielectric with a Al₂O₃ surface results in a decrease in the 3:4 ratio. The reactions with unattached Rh porphyrins and octylphosphonate-coated electrodes shed light on this disparity: with both coated TiO₂ and coated Al₂O₃ surfaces, application of a voltage results in a decrease in the 3:4 ratio. The use of bare TiO₂/Si electrodes with a RhTPP(I)(PPh₃) catalyst also results in a decrease of the 3:4 ratio upon application of a voltage. Together, these results indicate that a voltage-induced increase in the 3:4 ratio requires a specific chemical interaction between a TiO₂ surface and the Rh porphyrin, which can be blocked by the presence of an alkylphosphonate layer on TiO₂ or a PPh₃ ligand on the Rh porphyrin. The effect on the selectivity is large enough such that at maximum sub-breakdown voltage, **3** is the exclusively observed product. Exploiting voltage-induced surface–organometallic catalyst^{28,29} interactions may be a fruitful strategy for controlling selectivity in other reactions. In contrast, a voltage-induced decrease in the

3:4 ratio does not require a specific chemical interaction between the surface and the Rh porphyrin. The selectivity changes in this direction upon application of a voltage provided there is no TiO₂–Rh porphyrin interaction. This change is consistent with an electrostatic effect on the reaction in the polarized interfacial environment, as explained below.

On the basis of previously reported reactions of diazo substrates with Rh catalysts, a plausible mechanism for the reaction of **2** is outlined in Scheme 2. The reaction proceeds through a Rh carbenoid intermediate that either cyclopropanates the alkene to form a bicyclohexanone or electrophilically attacks the alkene to form a zwitterionic intermediate that subsequently rearranges to the cyclohexenone.³⁰ In a simple electrostatic model, if reaction of the Rh carbenoid intermediate were the product-determining step, a local electric field, *E*, would change the difference in activation barriers between the two pathways ($\Delta\Delta G^\ddagger$) by an amount equal to *E*· $\Delta\mu$, where $\Delta\mu$ is the difference in dipole moments between the two transition states. We propose that field–dipole interactions at the polarized interface favor product **4** (lower the 3:4 ratio) by preferentially stabilizing the activation barrier for **4** in the product-determining step.

In the parallel plate cell, *E* arises from the double layer charge density, charges on the underlying Si electrode that are balanced by electrolyte ions in the dielectric–electrolyte interfacial region when a voltage is applied to the cell. The magnitude and direction of *E* experienced by a Rh carbenoid intermediate are expected to fluctuate rapidly relative to the formation of product as a result of ion motion at the interface and orientational changes of the intermediate itself. A Rh carbenoid therefore experiences a distribution of local electric fields, some of which are aligned to form stabilizing interactions with a transition state dipole, while others are aligned to form destabilizing interactions. Stabilizing field–dipole interactions dominate the effect on selectivity because they accelerate the product-determining step. Assuming that the transition state for the formation of the zwitterionic intermediate is more polar than the transition state for cyclopropanation, field–dipole interactions favor formation of **4** (the 3:4 ratio decreases) because larger field–dipole stabilization is attained for the transition state to **4** than for the transition state to **3**.

The 3:4 ratio decreases at both positive and negative voltages for 1/Al₂O₃/Si electrodes. The ratio also decreases at nonzero voltages when unattached catalysts are used in the parallel plate cell even though they may adsorb on both the positive and the

negative electrodes. The electrostatic model described above can account for this symmetry provided that similar stabilizing field–dipole interactions are attainable at positive and negative electrodes.

Although E is dynamic on the molecular level, the average magnitude of E is proportional to the double layer charge density. If $E \cdot \Delta\mu$ contributes to $\Delta\Delta G^\ddagger$, the change in product ratio is expected to exhibit an exponential dependence on the double layer charge density. Unfortunately, the chemical complexity of the interface makes it difficult to measure double layer charge density directly in the parallel plate cell. Chronocoulometry measures the charge per unit area on the underlying Si electrode as a function of the voltage (Figure 3). This measurement does not provide double layer charge density directly because the charge density on the Si is balanced by a combination of charges in the double layer and accumulation of charges in the metal oxide layer. The amorphous Al_2O_3 or TiO_2 layers in the parallel plate cell can accumulate positive/negative charges by protonation/deprotonation of the oxide itself or coordinated H_2O molecules or by migration of electrolyte ions into the oxide.³¹ Oxide charging is evidenced by the relatively slow (several min) discharge observed upon stepping to 0 V after applying a nonzero voltage for multiple hours.

Oxide charging provides an explanation for features of the voltage-dependent selectivity changes in the parallel plate cell reactions that are otherwise difficult to reconcile with an electrostatic effect. In all cases, appreciable selectivity changes are not observed until a threshold voltage is applied despite the approximately linear increase in charge density with voltage measured by chronocoulometry. We propose that at subthreshold voltages, nearly all of the charge on the Si is balanced by oxide charging, resulting in very little double layer charge density and therefore a very small E to perturb the reaction. After the oxide becomes saturated with charge, additional voltage results in a significant increase in the double layer charge density, and effects on the selectivity appear. The amount of oxide charging at a particular voltage depends on whether Al_2O_3 , TiO_2 , or an oxide stack is used. While larger selectivity changes at lower voltages are observed for $1/\text{Al}_2\text{O}_3/\text{TiO}_2/\text{Si}$ electrodes as compared to $1/\text{Al}_2\text{O}_3/\text{Si}$ electrodes, the difference is not commensurate with the very large difference in charge density between the two electrodes (Figure 3). This result can be explained by a much higher charging capacity for an $\text{Al}_2\text{O}_3/\text{TiO}_2$ stack than for Al_2O_3 alone.

The maximum electrostatic effect on selectivity that can be achieved in the parallel plate cell is limited by the maximum attainable double layer charge density. Oxide charging attenuates double layer charging at a given voltage, and dielectric breakdown limits the maximum voltage that can be applied. Overcoming these limitations will require new designs for electrode–electrolyte interfaces or alternative interfaces that can be polarized by the application of a voltage. The larger selectivity changes observed with $1+5/\text{Al}_2\text{O}_3/\text{Si}$ and $\text{PSS}/1+5/\text{Al}_2\text{O}_3/\text{Si}$ electrodes (Figure 4) suggest that constructing interfaces with localized ionic functionality is a promising strategy. The use of alternative dielectrics with higher capacitance but a lower propensity to accumulate exogenous charges should enable the attainment of significantly higher double layer charge densities.

Although this study has focused on one reaction, the results are encouraging for the use of electrostatic effects to address challenges in selectivity. In reactions of similar diazoketone

substrates with a variety of transition metal catalysts, selective formation of a cyclohexenone product has proven elusive.²¹ Our results suggest that a Rh porphyrin favors cyclohexenone product **4** in an appropriate electrostatic environment. Increasing the preference for **4** beyond the maximum obtained here (a 3:4 ratio of 1:2) may be possible with the application of higher electric field strength. Moreover, for this reaction, voltage-induced selectivity changes in opposite directions are possible by simply changing the surface chemistry, indicating that polarized interfaces may be exploited in multiple ways to access different products. Utilizing other dielectric layers with enhanced properties should allow for further enhancement of the effect. In addition, other polarizable interfaces, such as an immiscible electrolyte–electrolyte interface,^{32,33} may enable use of field effects to control selectivity without the limitations of insulating oxides.

CONCLUSIONS

The selectivity of a Rh porphyrin-catalyzed carbene reaction occurring at a dielectric–electrolyte interface can be changed by the application of a voltage across the interface. The selectivity changes are consistent with two distinct phenomena that depend on the surface chemistry of the dielectric. For a TiO_2 surface, a voltage-induced Rh porphyrin– TiO_2 interaction changes the selectivity of the catalyst to favor the cyclopropanation product. For other surfaces tested, voltage-induced interfacial electric fields create field–dipole interactions that preferentially lower the activation barrier to the insertion product. The maximum strength of an electric field that can be applied to a molecular catalyst depends on the interfacial charge density that can be attained before dielectric breakdown. The development of interfaces designed for optimal charge density would further enhance the effects on selectivity.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data for all compounds, electrode characterization, current density traces, impedance spectroscopy, mass spectrometry, and additional control experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

mkanan@stanford.edu

Notes

The authors declare no competing financial interest.

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