Electrostatic catalysis–manipulating chemical reactions with electric fields
Reaction rate constants under the influence of external electric fields

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December 18, 2019

Our group

- Statistical mechanics research group:
  - *Electric field effect on chemical reaction rate*
  - Quantum-classical dynamics in the mapping bases
  - Calculating flammability limits of combustables

Motivation

- The effect of electric fields in electrochemistry (voltage applied to electrodes) is well studied by electrochemists.
- Effect of electric fields on non RedOx reactions has recently took over the imagination of some researchers.
- What about non-redux reactions?
- Stabilizing or destabilizing charge separated resonance contributors.
- Electrostatic effects are highly directional and quenched in polar media.
- Low polarity active site in which the substrate binds in an oriented manner.

Motivation

- Shaik, S., et al. (2004). "External Electric Field Will Control the Selectivity of Enzymatic-Like Bond Activations." Journal of the American Chemical Society 126(37): 11746-11749.
- Cpd I is an enzyme that can activate propene to perform either C=C epoxidation or allylic C-H hydroxylation.

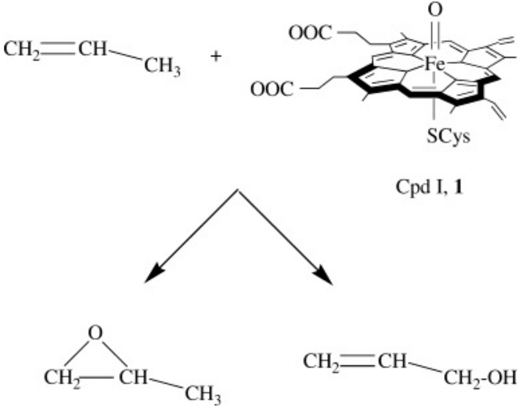

Figure: Structure of CPd I

Motivation

- Electric field calculations implemented in Gaussian 98 was used.
- Transition state energies are calculated and Cpd I is shown to be a non-regioselective reagent.
- An electric field along the S-Fe-O axes is shown to impart ragioselectivity depending on the field direction while in perpendicular directions no regioselectivity is predicted.
- Shaik, S., et al. (2016). "Oriented electric fields as future smart reagents in chemistry." Nature Chemistry 8: 1091.
- A perspective paper charting the horizon for possibilities with OEEF.
- Cytochrome P450 (Cpd I) catalyzes hydroxylation by an H abstraction and double bond epoxydation by an Fe=O attack.

Motivation

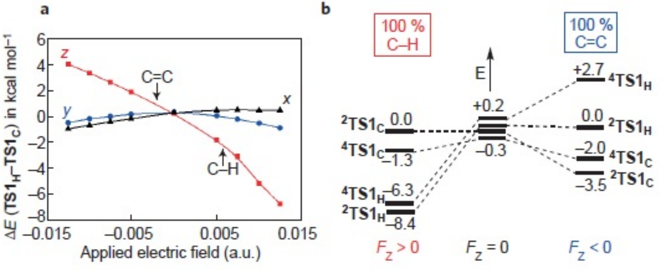

Figure: Electrostatic catalysis of a Diels-Alder reaction

- External field in the oxygen to sulfur direction prefers epoxidation while external field in the sulfur to oxygen drection prefers hydroxylation.

Motivation

- Aragons, A. C., et al. (2016). "Electrostatic catalysis of a Diels–Alder reaction." Nature 531: 88.
- Discusses the potential of oriented external electric fields (OEEF) to catalyze and control non-redox reactions and create selectivity.
- Designed a surface model system probing the Diels-Alder reaction and couple it with a scanning tunneling microscopy.
- Presence of an aligned electric field increased the frequency of single molecule junctions by 5 folds.
- Single molecule electrical measurements based on STM provide chemical coupling information averaged over thousands of collisions.
- Diels-Alder reaction, a bimolecular carbon-carbon bond-forming reaction which involves reagents of negligible polarity can be accelerated by OEEF.

Motivation

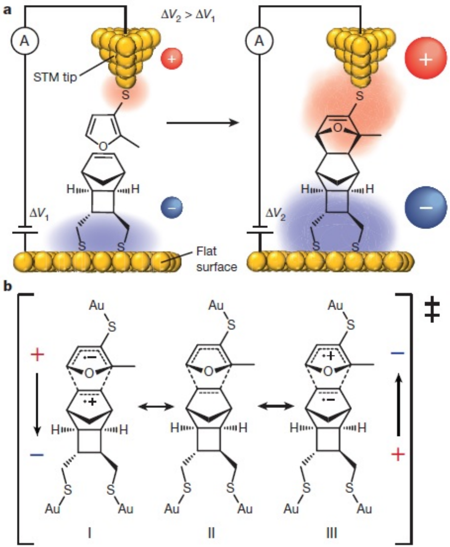

Figure: Selective bond activation of propene

Motivation

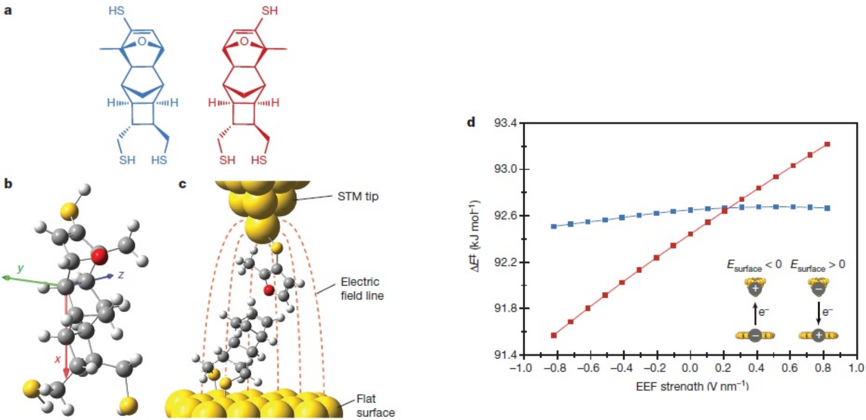

Figure:

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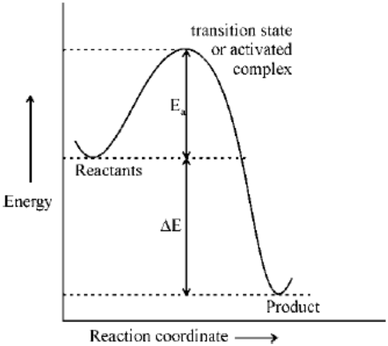
Motivation

- Gorin, C. F., et al. (2012). "An Electric Field-Induced Change in the Selectivity of a Metal Oxide-Catalyzed Epoxide Rearrangement." Journal of the American Chemical Society 134(1): 186-189.
- Gorin, C. F., et al. (2013). "Interfacial Electric Field Effects on a Carbene Reaction Catalyzed by Rh Porphyrins." Journal of the American Chemical Society 135(30): 11257-11265.
- Akamatsu, M., et al. (2017). "Electric-Field-Assisted Anion–π Catalysis." Journal of the American Chemical Society 139(19): 6558-6561
- Fried, S. D. and S. G. Boxer (2017). "Electric Fields and Enzyme Catalysis." Annual Review of Biochemistry 86(1): 387-415.

Motivation

- To orient molecules relative to an external field is impractical in most cases and un-economical in few cases where it is possible.
- We expect the difference between dipole moment and polarizability of reactants and the activated complex to cause stabilization and destabilization of the activated complex relative to reactants.
- Further we expect the molecules to become partially oriented and thus their collisions are no more random.
- Both the Change in activated complexes energy relative to the reactants and the directionality in reactant collisions can enhance or reduce chemical reaction rates.

Eyring theory

- 

(a) Exothermic reaction
- The average molecular speed in a single direction is $\bar{\dot{x}} = (\frac{kT}{2\pi m^*})^{1/2}$
- Average life time of the activated complex $\tau = \frac{\delta}{(\frac{kT}{2\pi m^*})^{1/2}}$

Eyring theory

- Rate constant of activated complex decomposition $k_I^\ddagger = \frac{1}{\tau}$
- Rate of activated complex decomposition:
  $w = k_I^\ddagger c^\ddagger = (\frac{kT}{2\pi m^*})^{1/2} \frac{1}{\delta} c^\ddagger$
- $w = (\frac{kT}{2\pi m^*})^{1/2} \frac{1}{\delta} K_c^\ddagger c_A c_B = k_{II} c_A c_B$
- $K_c^\ddagger = \frac{(q^\ddagger)}{q_A q_B} e^{-E_0^\ddagger/RT}$
- $k_{II} = \frac{kT}{h} \frac{(q^\ddagger)}{q_A q_B} e^{-E_0^\ddagger/RT}$

Electrostatic effect on reaction rate constant

- $k_{rel} = \frac{k(E{=}E')}{k(E{=}0)} = \frac{\frac{kT}{h}\left(\frac{(q^{\ddagger})(E{=}E')}{q_A(E{=}E')q_B(E{=}E')}\right)e^{-E_0^{\ddagger}/RT}}{\frac{kT}{h}\left(\frac{(q^{\ddagger})(E{=}0)}{q_A(E{=}0)q_B(E{=}0)}\right)e^{-E_0^{\ddagger}/RT}}$
- To calculate partition function at $(E = E')$, use $H(E = E') = H(E = 0) + \vec{\mu}\cdot\vec{E} + \frac{1}{2}\vec{E}\cdot\alpha\cdot\vec{E}$
- $H(E = 0) = H_{tr} + H_{rot} + H_{vib} + H_{elec}$
- $k_{rel} = \frac{e^{\frac{\alpha^{\ddagger}E'}{2kT}}\frac{\sinh\left(\frac{\mu^{\ddagger}E'}{kT}\right)}{\left(\frac{\mu^{\ddagger}E'}{kT}\right)}}{e^{\frac{\alpha_A E'}{2kT}}\frac{\sinh\left(\frac{\mu_A E'}{kT}\right)}{\left(\frac{\mu_A E'}{kT}\right)}e^{\frac{\alpha_B E'}{2kT}}\frac{\sinh\left(\frac{\mu_B E'}{kT}\right)}{\left(\frac{\mu_B E'}{kT}\right)}}$
- $k_{rel} = e^{\frac{(\alpha^{\ddagger}-\alpha_A-\alpha_B)E'}{2kT}}\frac{\frac{\sinh\left(\frac{\mu^{\ddagger}E'}{kT}\right)}{\left(\frac{\mu^{\ddagger}E'}{kT}\right)}}{\frac{\sinh\left(\frac{\mu_A E'}{kT}\right)}{\left(\frac{\mu_A E'}{kT}\right)}\frac{\sinh\left(\frac{\mu_B E'}{kT}\right)}{\left(\frac{\mu_B E'}{kT}\right)}}$
- $k_{rel} = e^{\frac{(\alpha^{\ddagger}-\alpha_A-\alpha_B)E'}{2kT}}\left(\frac{\mu_A\mu_B E'}{\mu^{\ddagger}kT}\right)\frac{\sinh\left(\frac{\mu^{\ddagger}E'}{kT}\right)}{\sinh\left(\frac{\mu_A E'}{kT}\right)\sinh\left(\frac{\mu_B E'}{kT}\right)}$

Electrostatic effect on reaction rate constant

- In the limit of small fields:
  $k_{rel} = [1 + (\frac{\Delta\alpha E'}{2kT}) + 1/2(\frac{\Delta\alpha E'}{2kT})^2][\frac{1+\frac{1}{6}(\frac{\mu^{\ddagger} E'}{kT})^2}{(1+\frac{1}{6}(\frac{\mu_A E'}{kT})^2)(1+\frac{1}{6}(\frac{\mu_B E'}{kT})^2)}]$
- $k_{rel} = [1 + (\frac{\Delta\alpha E'}{2kT}) + 1/2(\frac{\Delta\alpha E'}{2kT})^2][\frac{1+\frac{1}{6}(\frac{\mu^{\ddagger} E'}{kT})^2}{(1+\frac{1}{6}(\frac{\mu_A E'}{kT})^2+\frac{1}{6}(\frac{\mu_B E'}{kT})^2)}]$
- $k_{rel} =$
  $[1 + (\frac{\Delta\alpha E'}{2kT}) + 1/2(\frac{\Delta\alpha E'}{2kT})^2][1 + \frac{1}{6}(\frac{\mu^{\ddagger} E'}{kT})^2 - \frac{1}{6}(\frac{\mu_A E'}{kT})^2 - \frac{1}{6}(\frac{\mu_B E'}{kT})^2]$
- $k_{rel} \approx 1 + (\frac{\Delta\alpha E'}{2kT}) + \frac{1}{6}(\frac{\mu^{\ddagger} E'}{kT})^2 - \frac{1}{6}(\frac{\mu_A E'}{kT})^2 - \frac{1}{6}(\frac{\mu_B E'}{kT})^2$