# Functionalized Boron Nanoparticles: Characterization of Thiol-ene Click Chemistry

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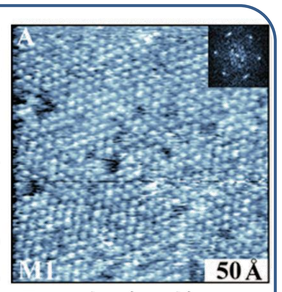
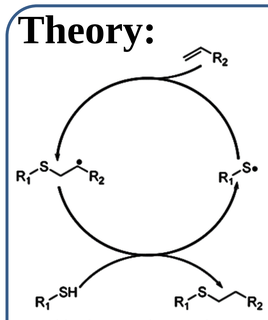
**Introduction:** Carboranes are a family of cluster compounds comprised of boron, carbon, and hydrogen that are being investigated in a number of applications, including self-assembling monolayers (SAMs), cancer treatment, and non-catalytic synthetic agents. Thiol-ene "click" chemistry between thiol-functionalized m-carborane and a variety of maleimide derivatives provides a facile path to a wide variety of functionalized boron nanoparticles. To characterize the reaction rate dependences, absorbance measurements were taken over time in a temperature controlled spectrophotometer starting with cysteine in place of carborane, as it is inexpensive and performs similarly.

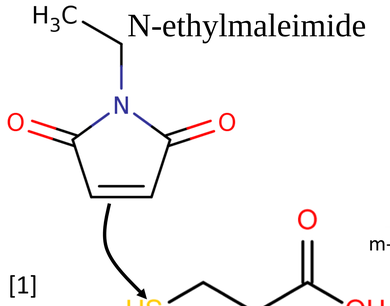



Example of a self assembling monolayer (SAM) [1]

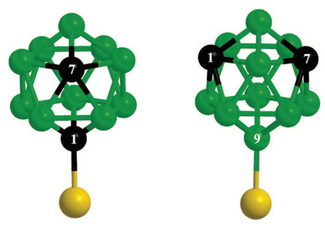
**Theory:**



"Click" Chemistry:
1) Initiation, 2) Propagation, 3) Termination [1]




L-cysteine



m-carborane-1-thiol m-carborane-9-thiol [2]

2nd Order Reaction

$$\frac{d[A]}{dt} = -k[A][B]$$

Rate Constant

$$\frac{1}{[A]} = kt + C$$

Arrhenius Equation

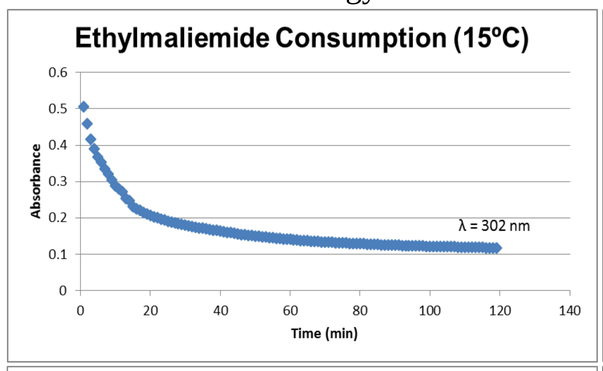
$$k = Ae^{\frac{-E_a}{RT}}$$

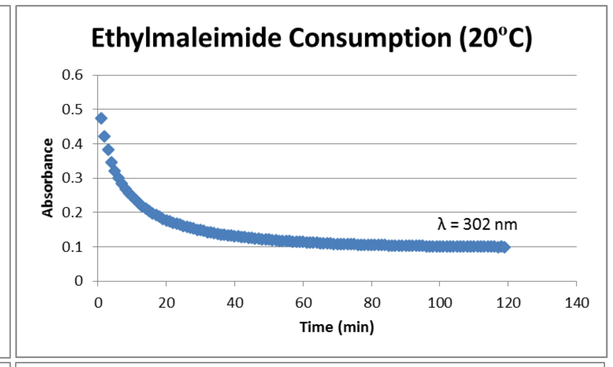
**Experimental Setup:** The UV-Vis spectrophotometer is connected to a circulator that controls the temperature of the reaction cuvette. The temperature can be reliably controlled from 15ºC to 35ºC by flowing antifreeze around the sample. At 40ºC, temperature control becomes unstable, lending to the 35ºC limit.

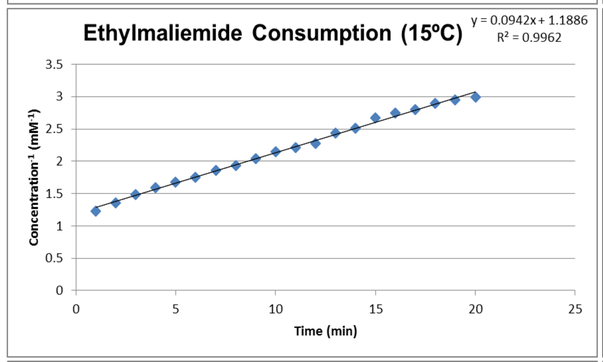

**Discussion:** Cysteine was chosen over carborane thiols as they are less expensive but are still representative of the carborane thiols. They react similarly with ethylmaleimide in a thiol-ene "click" reaction. The data show:

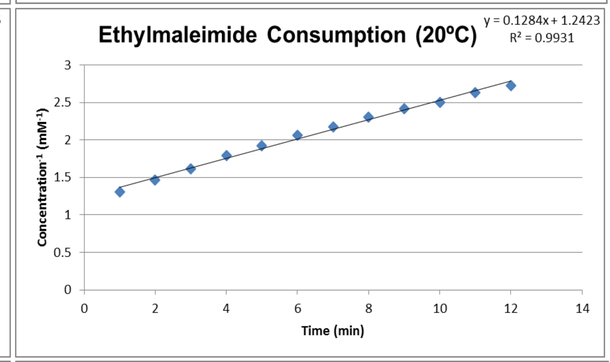
- The reaction is second order with a 0.034 $mM^{-1}s^{-1}$ change in the reaction constant, k, for a temperature change of 5ºC between 15ºC and 20ºC.
- Cysteine degrades in aqueous solution. A decomposition curve would provide valuable information as to whether the 0.1 end absorbance is a stoichiometric imbalance or equilibrium.
- The reaction between cysteine and ethylmaleimide has a maximum absorbance at 255 nm. Carbon-sulfur bonds absorb at 256 nm indicating the "click" reaction is present [3].
- Testing with carborane-thiol and ethylmaleimide at the same temperatures will be used to obtain comparable data for the activation energy and rate constants for this "click" reaction.

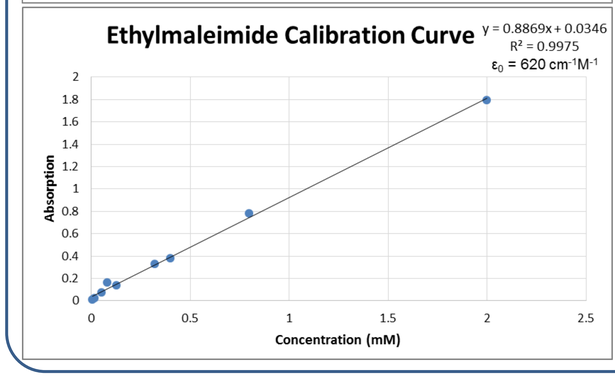
**Results:** The reaction kinetics of thiol-ene "click" between cysteine and ethylmaleimide chemistry shows a k of 0.094 ± 0.001 $mM^{-1}s^{-1}$ for 15ºC and 0.128 ± 0.003 $mM^{-1}s^{-1}$ for 20ºC. The activation energy was determined to be 17 ± 3.3 kcal/mol.

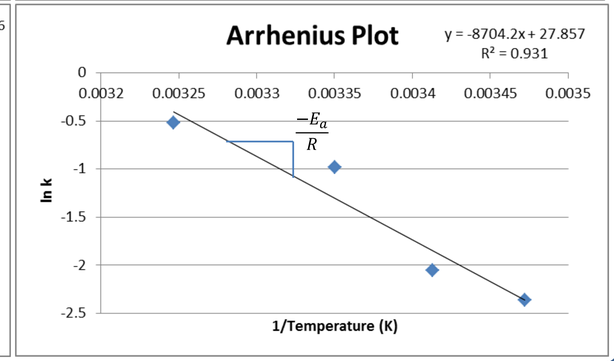



**Future Research:** Further testing will be conducted with m-carborane-1-thiol and m-carborane-9-thiol in order to further quantify the reaction rate constant, k, and the activation energy of the thiol-ene "click" reaction at temperature ranging from 15ºC to 35ºC. Electron density modelling will elucidate the structure of the complexed ethylmaleimide and cysteine and aid in the identification of the preferential bonding. Future work will also include infrared spectroscopy to determine all reaction products.

**References:** [1] Hohman, N. J., P. Zheng, and P. Weiss (2009). " Self-assembly of Carboranethiol isomers on Au{111}." ACS, 2009; 3(3): 527-536.

[2] Grimes, Russell N. *Carboranes*. New York: Academic, 1970. Print.

[3] Pacheco, B., Kordyban, S. Sigma Aldrich. *Material Matters*. Precise Nanoparticles for Optoelectronics Applications. 7:1

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