Green Catalytic Activation of H_2O_2 by Organometallic Compounds

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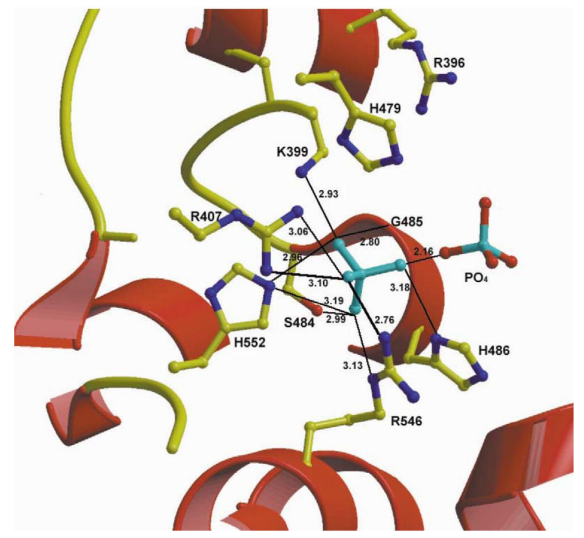
Abstract

Organoselenide and organotelluride compounds are of great interest in "green" chemistry because of their ability to activate hydrogen peroxide. Hydrogen peroxide by itself is a slow oxidizing agent, but when activated, it is kinetically useful. While the organoselenide and telluride dendrimers prepared by Detty and colleagues have shown significant catalytic activation of H_2O_2, their catalysts were not water soluble and were prone to selenoxide syn-elimination. Various diphenyl selenide and diphenyl telluride species are being investigated because they lack β-hydrogens, and hold the potential to be water soluble when structurally modified. Using gas chromatography, the catalytic rate of H_2O_2 activation is evaluated with these different species. A blank rate is determined initially in order to standardize the efficiency of each catalyst. Diphenyl selenide does not show an increased rate of catalytic activity while diphenyl telluride shows a modest degree of catalysis. Pre-oxidation of diphenyl selenide results in no increase in the rate of H_2O_2 activation over the blank rate.

Natural Inspiration for Project

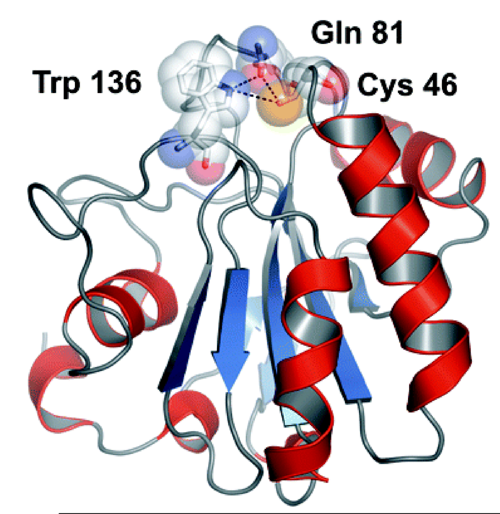
Vanadium Bromoperoxidase (V-BrPO):



Littlechild, J.; Garcia-Rodriguez, E. *Coordination Chemistry Reviews*, **2003**, *237*, 65-76.

- Enzyme found in specific algae, sponges, and other marine organisms
- Vanadium active site reacts with H_2O_2
- Oxidizes NaBr in sea water to "Br+" species to make halogenated metabolites

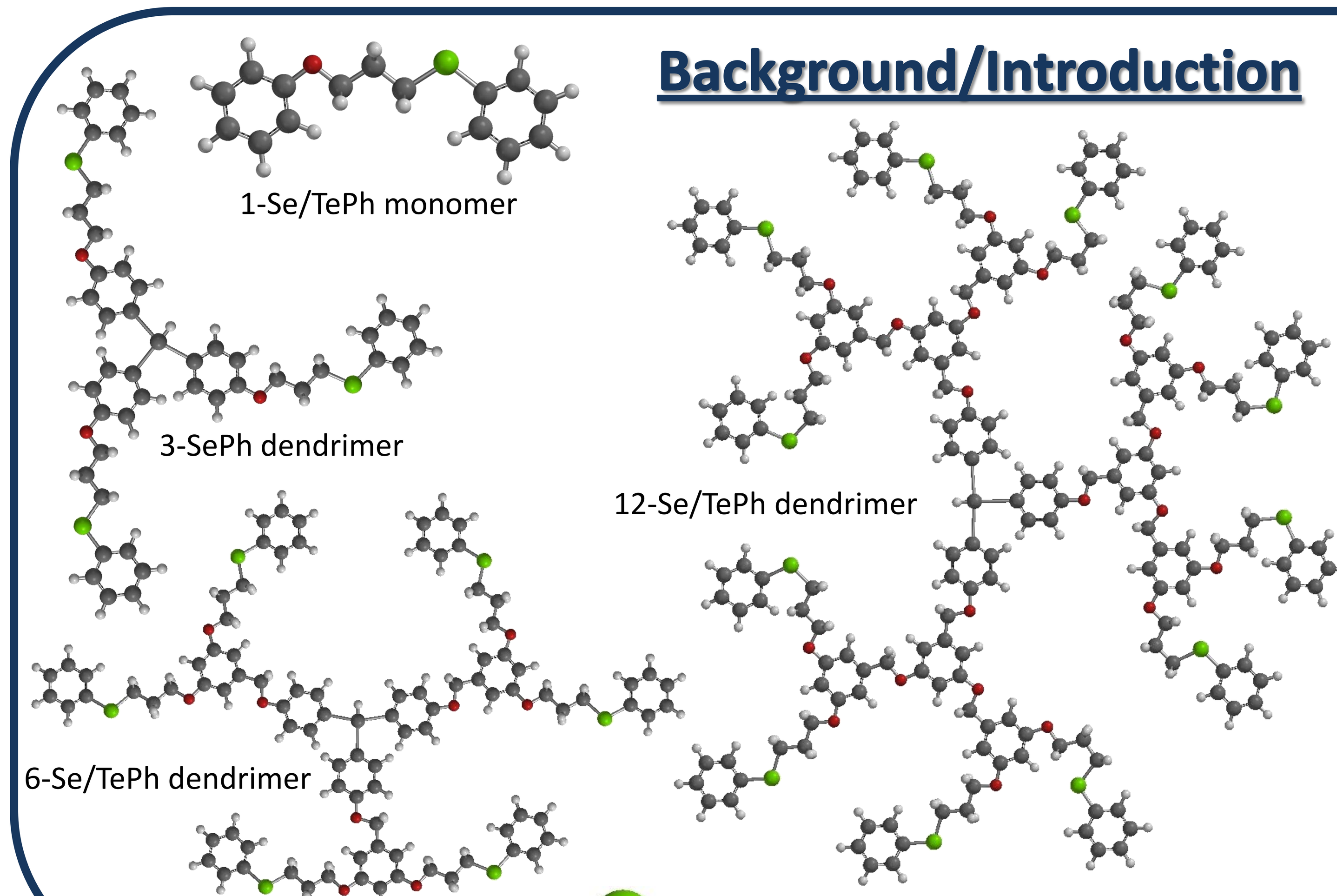
Glutathione Peroxidase (GPx):



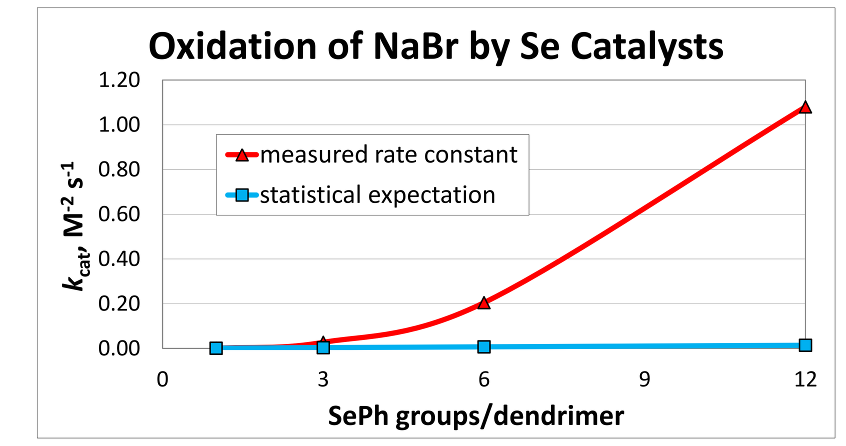
Scheerer, P.; Borchert, A.; Krauss, N.; Wessner, H.; Gerth, C.; Hohne, W.; Kuhn, H.; *Biochemistry*, **2007**, *46*, 9041–9049.

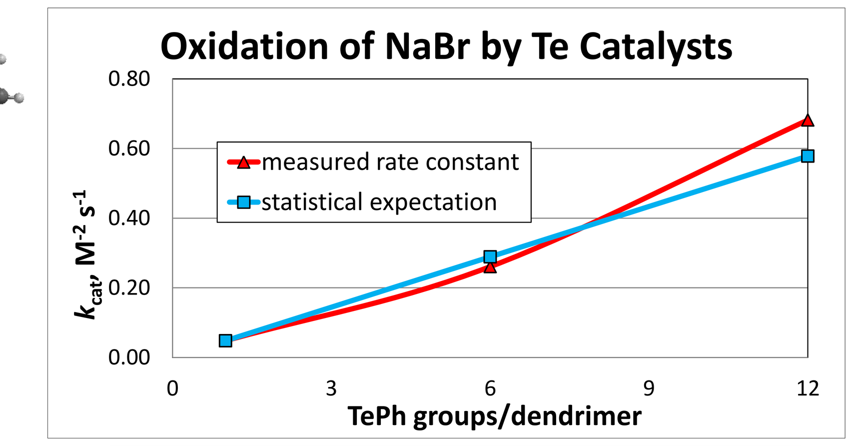
- Mammalian antioxidant enzyme containing a selenocysteine active site
- Selenium active site reacts with peroxides, ridding them from the body

Background/Introduction



= selenium or tellurium atom

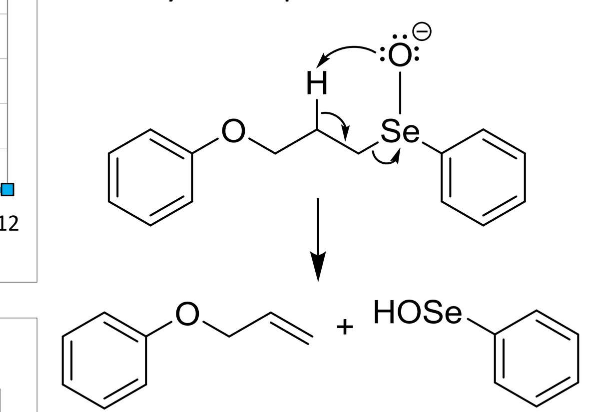




1. Francavilla, C.; Drake, M. D.; Bright, F. V.; Detty, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 57-67.
2. Drake, M. D.; Bright, F. V.; Detty. M. R. *J. Am. Chem. Soc.* **2003**, *125*, 12558-12566.

But...

- Catalysts are not H_2O soluble
- Catalysts are prone to elimination



Goal of the Project

1. **Make Se and Te catalyst that are H_2O soluble**
2. **Make Se and Te catalysts that do not possess β-hydrogens**

Oxidation Setup

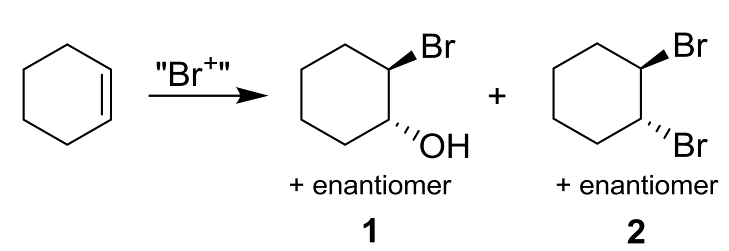
Two-phase system

NaBr, H_2O_2, cyclohexene, pH 6.0 buffer, CH_2Cl_2 with internal standard, 25.0 °C

Br^- is oxidized

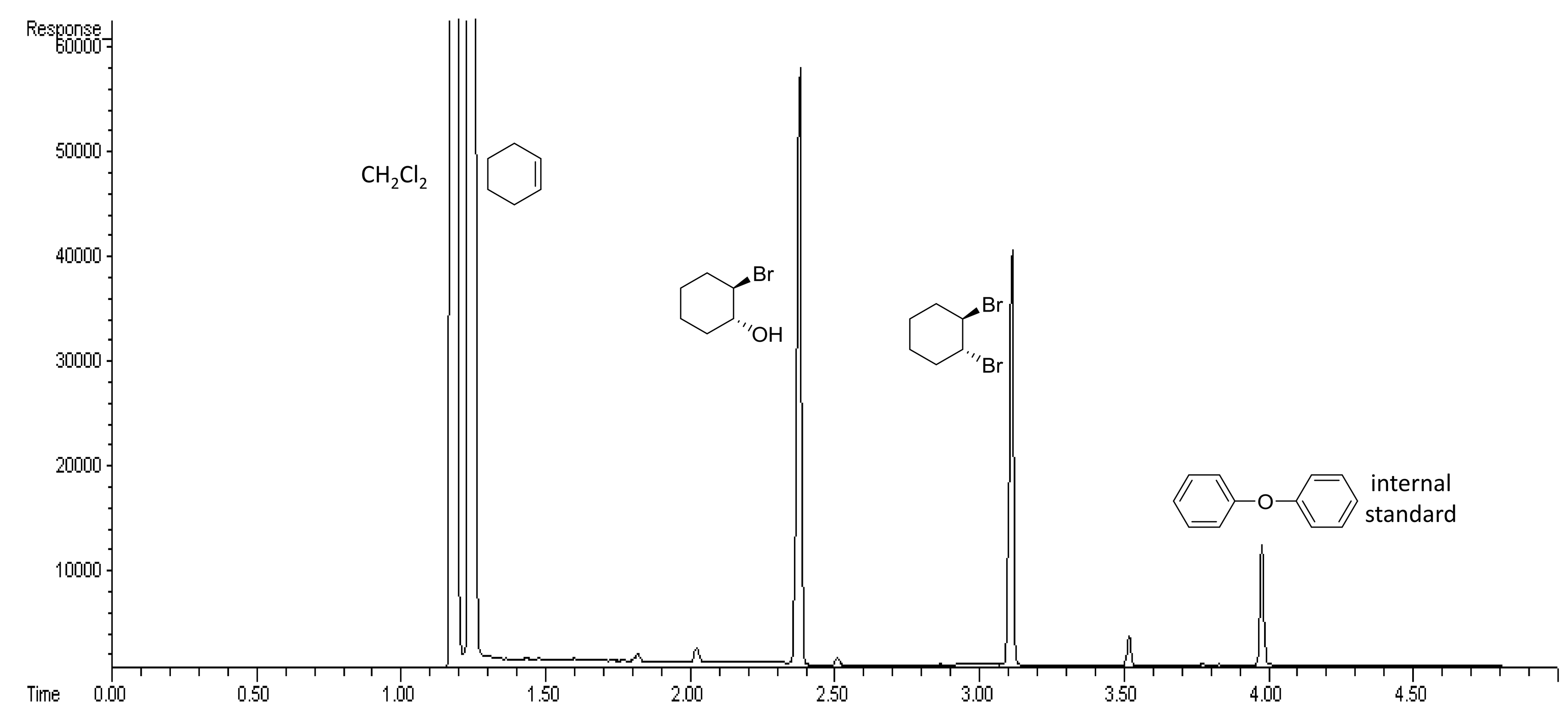
$$NaBr + H_2O_2 \longrightarrow \text{"}Br^{+}\text{"} + 2\,^{-}OH \quad (Br_2, BrOH, Br_3^-)$$

"Br+" is captured by cyclohexene



- formation of **1** and **2** is monitored by GC
- samples are withdrawn every 5-10 minutes

Typical Gas Chromatogram



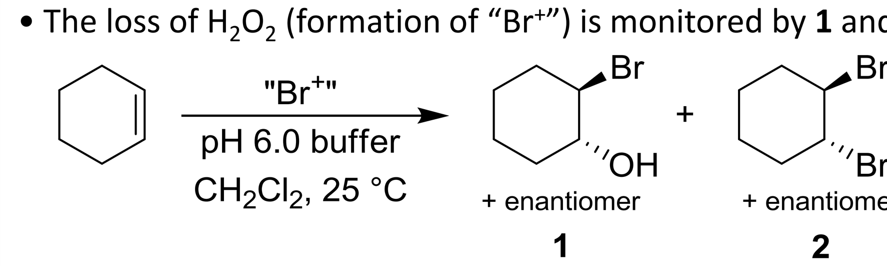
Oxidation Reaction Kinetics

Reactions

blank reaction = $NaBr + H_2O_2 \longrightarrow \text{"}Br^{+}\text{"} + 2\,^{-}OH$ (Br_2, BrOH, Br_3^-)

- Reaction is first-order in H_2O_2, zero-order in NaBr

- The loss of H_2O_2 (formation of "Br^+") is monitored by **1** and **2**



Kinetics

blank rate = $k_{blank}[H_2O_2]$

$\ln[H_2O_2]_t = -k_{blank}t + \ln[H_2O_2]_0$

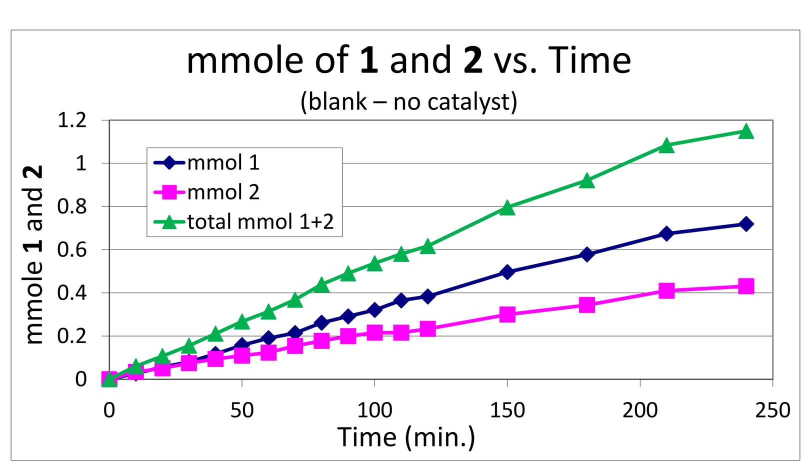
$\ln[\mathbf{1+2}]_t = -k_{blank}t + \ln[\mathbf{1+2}]_0$

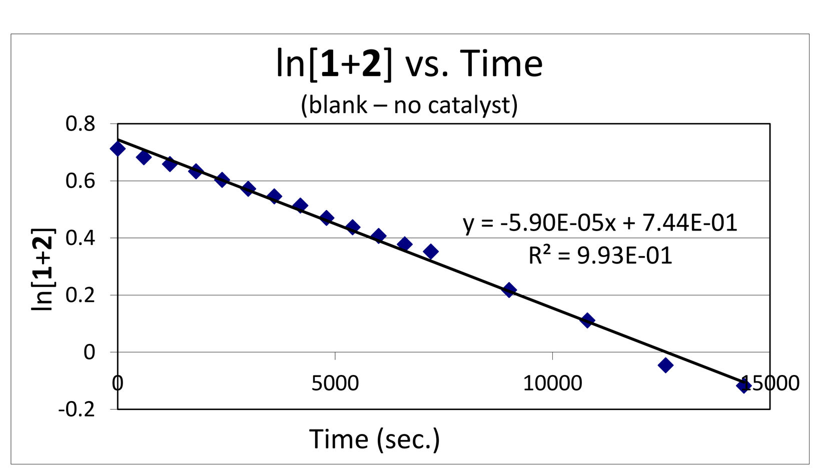
y = (m)(x) + b

- the negative slope of the line is the rate constant

Observed rate of a catalyzed reaction = blank reaction rate + catalyzed reaction rate = $k_{obs}[H_2O_2]$

Blank Reaction Results



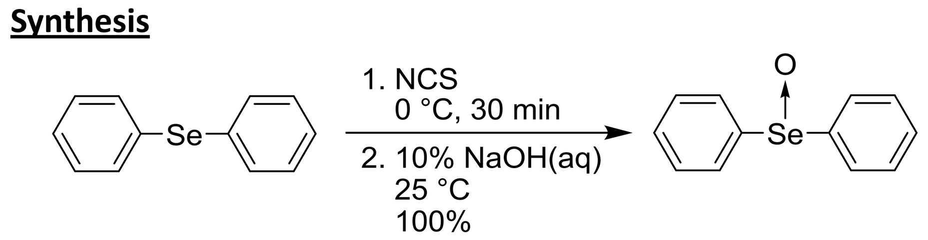


k_{obs} = Average of 5 trials = (4.17 ± 0.70) x 10^{-5} s^{-1}

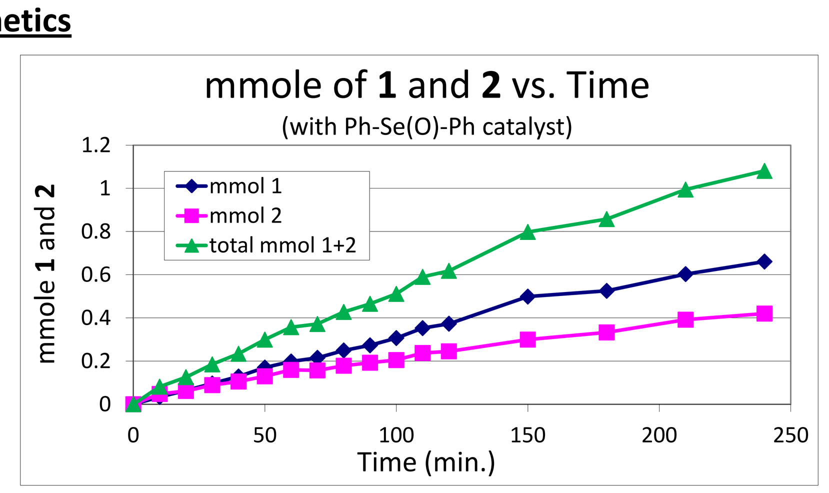
Diphenyl Selenoxide Results

- Diphenyl selenide is commercially available
- Se oxidizes slowly in H_2O_2, so it was pre-oxidized

Synthesis



Kinetics



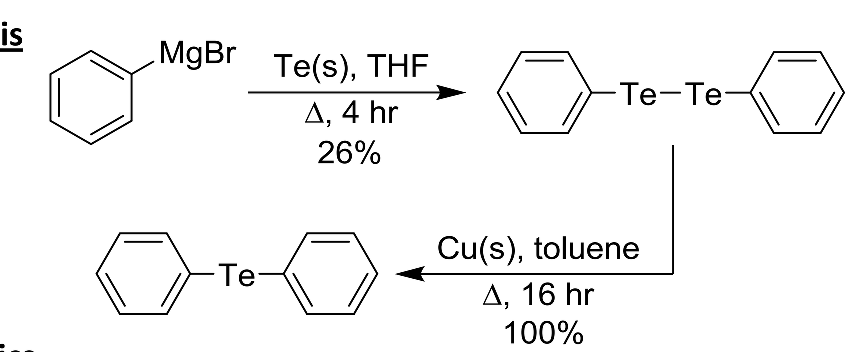
k_{obs} = Average of 3 trials = (4.77 ± 0.75) x 10^{-5} s^{-1}

k_{cat} = (1.26 ± 3.69) x 10^{-4} $M^{-2}s^{-1}$

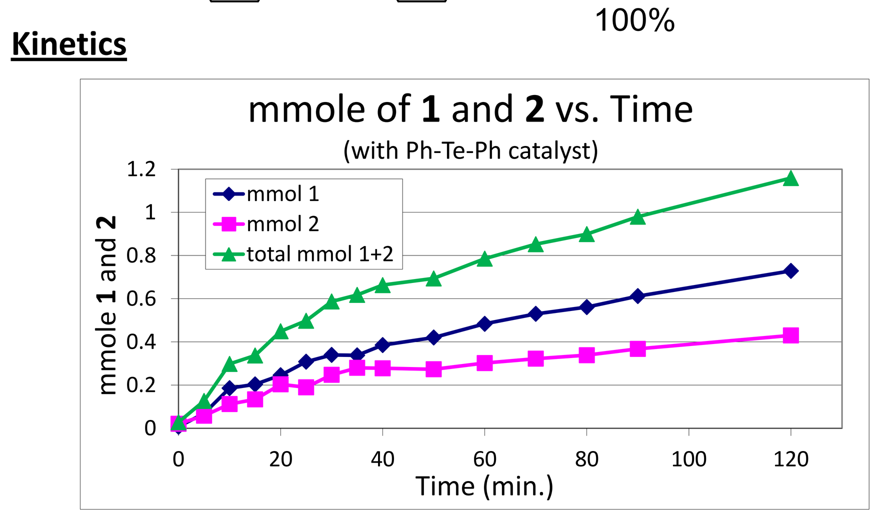
Diphenyl Telluride Results

- Diphenyl telluride is not commercially available, it must be synthesized
- Te oxidizes rapidly in H_2O_2, it was not pre-oxidized

Synthesis



Kinetics



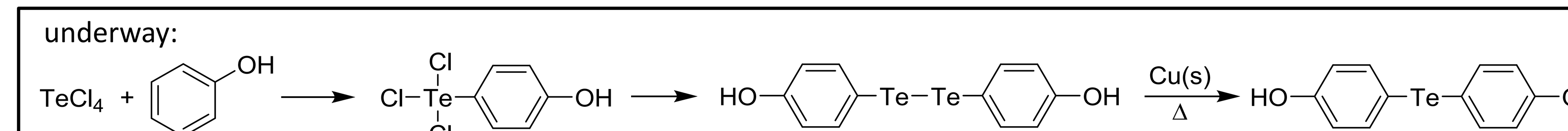
k_{obs} = Average of 3 trials = (8.15 ± 1.47) x 10^{-5} s^{-1}

k_{cat} = (9.66 ± 4.45) x 10^{-4} $M^{-2}s^{-1}$

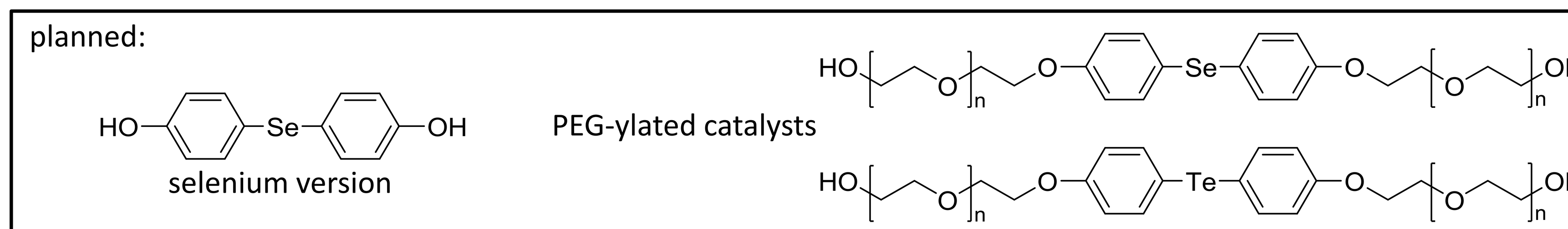
Future Work

1. Synthesis of Potentially Water Soluble Catalysts

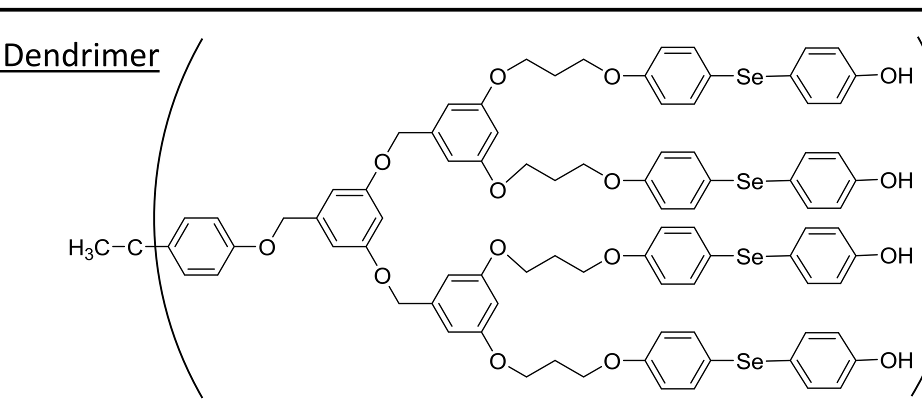
underway:



planned:



2. Incorporation Into a Dendrimer



Acknowledgments

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