Mechanistic Studies of Thiol Oxidation by $^{19}\text{F NMR}$

Kaitlyn Margison, Jean-Philippe R. Chauvin & Derek A. Pratt*
Department of Chemistry, University of Ottawa, Ottawa, ON, Canada

**Introduction**

- The intermediate products of thiol oxidations have been found to play a role in a growing number of chemical and biological processes such as signal transduction, protein folding and enzymatic processes.
- For example, glutathione, a tripeptide containing a nucleophilic thiol, is present in high concentration (up to ~5mM) in cells and offers a line of defense against oxidative stress.
- The process of thiol oxidation is much more complex than a 'textbook reaction'. This is presumably due to the high reactivity of sulfenic and sulfenic acids towards oxidation, rendering it nearly impossible to isolate.
- The isolation and characterization of these intermediates has yet to be determined.
- Previous research in our laboratory enabled the synthesis of a persistent sulfenic acid; 9-triptocene sulfenic acid.
- The high steric hindrance of the triptycene backbone plays an important role as a protecting group in the stabilization of the sulfenic acid. This structure will enable the complete characterization and kinetic analysis of thiol oxidation reactions.
- Monitoring the reaction kinetics by $^{19}\text{F NMR}$ is a more efficient way to collect kinetic data while minimizing product handling and cost.
  - $d_2\text{MeOH} = \$150/5g$

**Synthesis of Triptycene Thiol Oxidation Products**

- Synthesis of the targeted fluorinated $t$-butyltriptocene will enable the production of the thiol, sulfenic acid and sulfenic acid standards.

**Synthesis of Fluoro-Triptycene Sulfenic Acid**

- Above are the authentic standards to be synthesized and analyzed through $^{19}\text{F NMR}$.

**Reaction Kinetics by $^1\text{H NMR}$**

- Figure 1. At $t=0$ only thiol is observed, but as the oxidation continues to $t=240\text{min}$, four well separated peaks are observed. Each peak is labeled according to the observed thiol oxidation product recorded NMR. This obvious separation challenges the 'textbook reaction' stigma and prompts further understanding of the oxidation. A similar, yet more informative analysis is expected to be achieved through $^{19}\text{F NMR}$.

**Kinetic Data**

**Future Work**

**References**


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