2007

Photochemical Production of MicromolarSuperoxideStandards in Aqueous SolutionT

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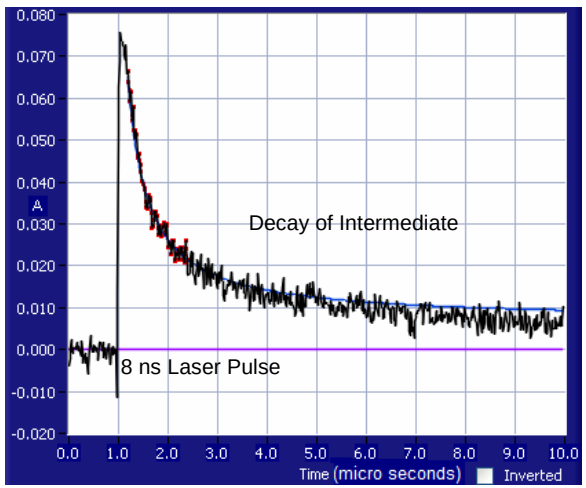
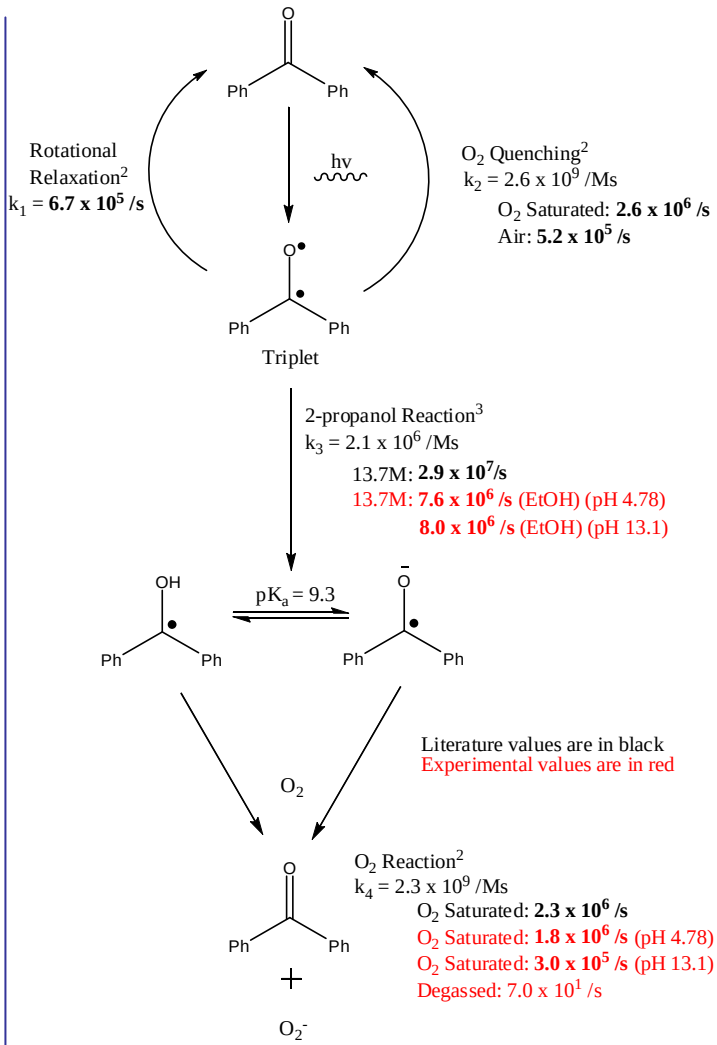
Introduction

Superoxide (O_2^-) is a reactive free radical that rapidly undergoes disproportionation to hydrogen peroxide and oxygen. This property makes preparation of superoxide standard for instrument calibration difficult. McDowell et al. (1983) showed photolysis of ketone and alcohol as a convenient method to generate superoxide through triplet and radical intermediates reacting with molecular oxygen. This study expands on this past work and investigates detailed mechanism of the reaction.

Laser Flash Photolysis

Laser flash photolysis was used to investigate the decay of triplet and radical intermediates as they react with oxygen. A Nd-YAG laser at 355 nm was used as the excitation source. Benzophenone and ethanol solution was used to generate benzophenone triplet and benzoradicals as shown in the figure to the right.

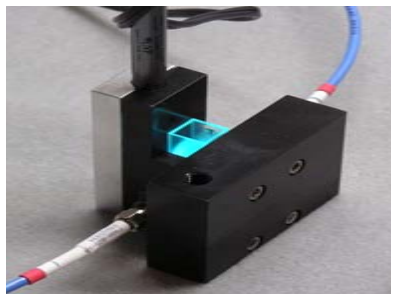


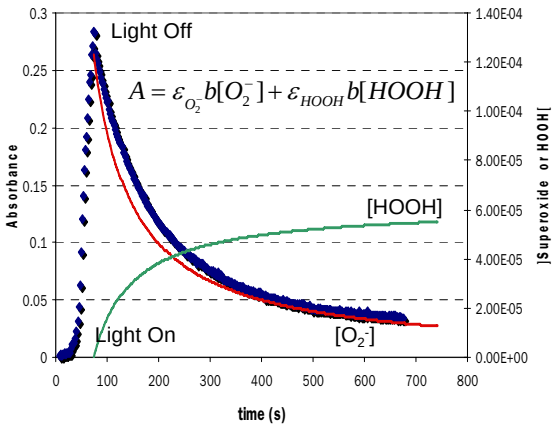


$$O_2^- \text{ yield} \approx \frac{k_3[EtOH]}{k_3[EtOH]+k_1+k_2[O_2]} \approx 0.70\,(O_2 \text{ Saturated})\,(13.7M\ EtOH)$$

Continuous Photolysis

Acetone and ethanol solution was irradiated with 256 nm mercury lamp, and the absorbance of superoxide and hydrogen peroxide is measure at 240 nm using UV/Vis Spectrophotometer.





This work confirms the mechanism of the production of superoxide through photolysis of ketone in the presence of alcohol, and provides a portable source of superoxide standard in micromolar concentration.

Reference

1. McDowell, M. S.; Bakac, A.; Espenson, J. H.; *Inorg. Chem*. **1983**, 22, 847-848.
2. Canonica, S.; Hellrung, B.; Wirz, J.; *J. Phys. Chem. A* **2000**, 104, 1226-1232.
3. Shield, S. R.; Harris, J. M.; *Anal. Chem*. **1998**, 70, 2576-2583.