Kinetics and mechanism of the sensitized photodegradation of lignin model compounds

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Supporting Information: **Derivation of expression to describe k_T**
    Sample transient signals obtained by laser flash photolysis

Derivation of expression to describe k_T

The following scheme was used in the development of an expression to quantify k_T. The derivation of this expression follows.

$$P_T \xleftarrow{k_T[S]} \text{sens} * \xrightarrow{k_{O_2}[O_2]} {}^1O_2 \xrightarrow{k_{solv}+k_{tot}[S]} P_{{}^1O_2}$$
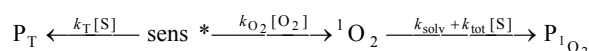
Kinetic model for measuring lignin model compound interaction with triplet sensitizer. O_2 is ground state molecular oxygen, ${}^1O_2$ is singlet oxygen, S is substrate, P_T is the product formed through reaction of S and sens* where sens* is excited state sensitizer, P_{1O2} is the product formed through reaction of S and ${}^1O_2$, k_{O2} is the rate constant for the formation of ${}^1O_2$ by the interaction of O_2 and excited state sensitizer, k_T is the rate constant for the interaction of excited state sensitizer with S that results in quenching or reaction, k_{solv} is the rate constant for deactivation of ${}^1O_2$ by solvent, k_{tot} is the sum of k_{phys}, and k_{rxn}, which are the rate constants for physical quenching by S, and chemical reaction with S, respectively.

The differential equation describing the changes in $[{}^1O_2]$ versus time for this model is given in equation 1.

$$\frac{d[{}^1O_2]}{dt} = k_{O_2}[O_2][\text{sens*}] - ((k_{solv}+k_{tot}[S])[{}^1O_2]) \tag{1}$$

The time-dependent concentration of triplet sensitizer is given by equation 2.

$$[\text{sens*}]_t = [\text{sens*}]_0\, e^{-(k_{O_2}[O_2]+k_T[S])t} \tag{2}$$

Inserting equation 2 into equation 1, rearranging, and integrating allows one to describe $[{}^1O_2]$ according to equation 3.[1]

$$[{}^1O_2] = \frac{[\text{sens*}]_0}{k_{solv}+k_{tot}[S]}\left(\frac{k_{O_2}[O_2]}{k_{O_2}[O_2]+k_T[S]}\right) \tag{3}$$

The area (A) under each transient signal is directly proportional to $[{}^1O_2]$, and was calculated at varying substrate concentrations. By dividing the relative ${}^1O_2$ concentration
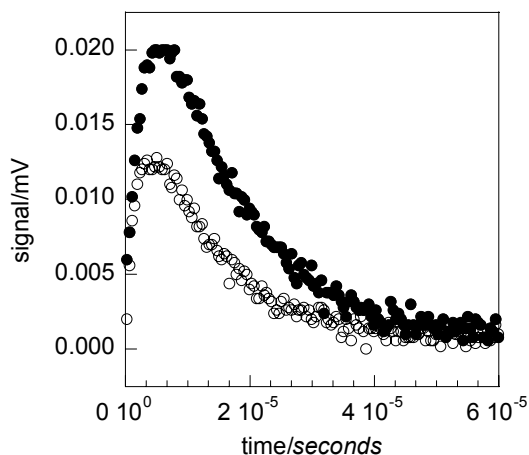
in the absence of substrate (A_0) by the relative $^1O_2$ concentration in the presence of substrate (A_S) equation 4 is obtained

$$\frac{A_0}{A_S} = \frac{(k_{solv} + k_{tot}[S])(k_{O_2}[O_2] + k_T[S])}{k_{solv}k_{O_2}[O_2]} \tag{4}$$

When $k_{tot}[S] \ll k_{solv}$, as is observed in the degradation of the neutral models, equation 4 is simplified to equation 5.

$$\frac{A_0}{A_S} = 1 + \frac{k_T}{k_{O_2}[O_2]}[S] \tag{5}$$

Sample $^1O_2$ transient signals obtained by laser flash photolysis

Transient signals showing the growth and decay of $^1O_2$ phosphoresence emission determined by laser flash photolysis for dimer **2** (0 mM, ● and 21.6 mM, ○) in EtOH using perinaphthenone as a sensitizer.

1   J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill Inc., New York, 2nd, 1995, 281 pp.