

Kinetics and mechanism of the sensitized photodegradation of lignin model compounds†

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The kinetics of the sensitized photodegradation of a variety of well-defined lignin model compounds was studied to determine the mechanisms responsible for lignin's photochemically-mediated oxidation. Monomeric and dimeric models representing lignin's phenolic end groups and nonphenolic dimers representing its inner core were studied. It was determined that the rate constants for the reaction of the deprotonated phenolic models with singlet oxygen ($^1\text{O}_2$) range from 0.96 to $7.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The models were substituted with zero, one, or two electron-donating methoxy groups on both aryl rings and, while the rate constants showed little dependence on the substitution of the nonphenolic ring, the rate constants increased dramatically with increasing methoxy substitution of the phenol. Reaction between these deprotonated models and $^1\text{O}_2$ is thus proposed to occur at the phenolate ring. Under neutral conditions, it was observed that the phenolic models react with excited state sensitizer, with this reaction also occurring at the phenol ring. The sum of the rate constants for quenching of and reaction with excited state sensitizer by lignin model compound ranges from 5.4 to $75 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This study corrects previous reports that attribute the sensitized degradation of neutral lignin model compounds to reaction with $^1\text{O}_2$. A nonphenolic aromatic ketone inner-core model was observed to undergo direct photolysis, and its reduced analog was not degraded by direct photolysis or reaction with $^1\text{O}_2$ or excited state sensitizer. The oxidized inner-core model was also shown to be able to act as a sensitizer for the degradation of a phenolic lignin model compound.

Introduction

Lignin comprises about 30% of the dry weight in vascular plants and is a core component of aquatic natural organic matter derived from terrestrial sources.^{1,2} Despite lignin's recalcitrance, it is degraded during transport to marine environments, as it is not present in the ocean in quantities proportional to its riverine export.^{1,3} Photooxidation is believed to be partly responsible for its degradation.³⁻⁶ To better understand the degradation and therefore, cycling, of aquatic organic carbon, we have conducted studies on the photochemically-mediated oxidative degradation of the lignin component of aquatic organic carbon.

Others have also been interested in the photochemical oxidation of lignin because of lignin's role in the photoyellowing of paper and its removal during the pulping process, which has proven to be notoriously difficult. Photochemical oxidation is an option for environmentally benign delignification.

Several photochemically-mediated mechanisms including direct photolysis, reaction with hydroxyl radical, singlet oxygen ($^1\text{O}_2$), and reactive triplet species are believed to be important in lignin's oxidation,⁷ but because lignin's structure is irregular and only partly defined, the contribution of each reaction pathway to lignin's degradation is not well understood. An added complication is the possibility of competing degradation pathways, even under controlled laboratory experiments. For example, lignin⁸⁻¹² and lignin model compounds^{13,14} have been shown to react with photochemically generated $^1\text{O}_2$ and lignin is known to react with thermally generated $^1\text{O}_2$.¹⁵ Other studies, however, have shown that lignin-like methoxyphenols quench and react directly with excited state sensitizers, like the ones used to sensitize the formation of $^1\text{O}_2$.¹⁶⁻¹⁸

Because lignin structures are reactive toward both $^1\text{O}_2$ and the triplet sensitizers used to generate $^1\text{O}_2$, studies that show the

transformation of lignin and lignin model compounds under $^1\text{O}_2$ -forming conditions must be regarded with caution. For example, it has been shown that photochemical degradation of lignin⁸ and lignin model compounds^{13,14} does not occur in the absence of sensitizer, and this has been taken as good evidence of singlet oxygen's participations in the reaction. However, studies have not been conducted in the presence of sensitizer and absence of oxygen. Because removal of the sensitizer prevents reaction with both $^1\text{O}_2$ and excited state sensitizer these pathways are not distinguished by these experiments.

It has been shown that lignin's photodegradation in the presence of Rose Bengal (a $^1\text{O}_2$ sensitizer) slows after 4–8 h, probably because the phenolic outer portion of the lignin polymer is degraded faster than the inner core.¹² This interesting finding reshaped our paradigm for thinking about lignin's photodegradation and inspired us to conduct well-defined laboratory experiments on lignin model compounds that represent the inner and outer portion of lignin in order to explain observations seen in the degradation of isolated lignin.

Thus, we have studied the degradation of a suite of lignin model compounds by different photochemical mechanisms, including direct photolysis, reaction with $^1\text{O}_2$, and reaction with excited state sensitizer. We have also made a cursory examination of lignin's proclivity to sensitize its own degradation. Monomeric and dimeric phenols were used as models of the outer portion the three-dimensional lignin polymer, and dimeric nonphenolic models were used to study lignin's inner core.

Lignin is characterized by a β -O-4 linkage that joins the β -C of a phenylpropanoid chain to the oxygen of a phenoxy ring, with the lignin polymer continuing *para* to this linkage. Generally, these aryl rings can have methoxy substituents *ortho* to the phenol's hydroxyl group, and the number of methoxy groups is indicative of the lignin's origin. Doubly substituted rings represent lignin's syringyl units (derived from hardwood), singly substituted rings represent lignin's guaiacyl units (derived from hardwood and softwood), and unsubstituted rings represent lignin's hydroxycinnamyl units (derived from grasses).^{19,20}

† Electronic supplementary information (ESI) available: Derivation of expression to describe k_T ; sample transient signals obtained by laser flash photolysis. See <http://www.rsc.org/suppdata/pp/b4/b416956e/>

We studied phenolic dimers that model lignin's end groups and have a guaiacyl phenylpropanoid group joined by a β -C-O linkage to a hydroxycinnamyl, guaiacyl, or syringyl phenoxy ring (**1**, **2**, and **3**, respectively). We also studied phenolic monomers that represent lignin's hydroxycinnamyl, guaiacyl, and syringyl units (**4**, **5**, and **6**, respectively). To study lignin's inner core, we studied ethyl-protected nonphenolic dimers prepared from guaiacyl precursors with either an oxidized (**7**) or reduced (**8**) chain linking the two aryl rings. Our aim is to use kinetic analyses to better understand the mechanism of the photochemical degradation of these models.

Experimental

Chemicals

Sodium borohydride, *n*-butylamine, copper(II) bromide, iodoethane, furfuryl alcohol (FFA), perinaphthenone and Rose Bengal were purchased from Aldrich. Acetovanillone, 4-hydroxyacetophenone, 3,5-dimethoxy-4-hydroxyacetophenone, guaiacol, 2,6-dimethoxyphenol, paraformaldehyde, and *p*-nitroanisole were purchased from Acros. Benzoyl chloride was purchased from Avocado. Bromine was purchased from Fisher. Phenol was purchased from Spectrum. Potassium carbonate was purchased from Mallinckrodt. Ethanol-*d* was purchased from Cambridge Isotope Laboratories. Basic ethanol (90 mM NaOEt in EtOH) was prepared by dissolving Na metal in EtOH. All solvents were ACS grade or higher and all EtOH was 200 proof.

Synthesis of lignin model compounds

The lignin model compounds were prepared according to literature procedures. End-group dimers **2–3** and inner-core model **7** were synthesized according to the procedure of Crestini and D'Auria¹⁴ and Kawai *et al.*²¹ and matched published ¹H NMR spectra. Dimer **1** was prepared in the same manner as **2** and **3**, substituting phenol for guaiacol or dimethoxyphenol, and its purity was confirmed by ¹H NMR and HPLC.²² End-group monomers **4–6** and inner-core model **8** were prepared by reducing the corresponding ketones with NaBH₄ and their purity was confirmed by ¹H NMR and HPLC. The dimeric phenols were studied as a mixture of threo and erythro diastereomers. The ratios of diastereomers were found to be 74 : 26, 50 : 50, and 65 : 35 for **1**, **2**, and **3** respectively, based on ¹H NMR or HPLC analysis. The major isomer is tentatively assigned as *threo* based on the work of others.^{21,23} The photochemical reactivity of these diastereomers was observed to be non-stereoselective.

Determination of pK_a for lignin model compounds

The pK_a of each phenolic model was determined by conducting a spectrophotometric titration. The absorbance of solutions containing lignin model compound (200 μ M) in six buffers varying in pH from 7 to 12 was recorded on a Jasco V-530 spectrophotometer. The absorbance at a peak maximum (240–250 nm) was plotted against the pH of the solution and a curve fit yielded the pK_a of each model (Table 1).

Photochemical studies

For the direct photolysis experiments, test tubes containing lignin model compound (100 μ M) in neutral or basic ethanol were arranged on a turntable below four Pyrex-filtered 175 W medium pressure Hg-vapor lamps (LumaPro, GE HR175A39/CP bulbs). Aliquots were removed at five or more timepoints over 30 minutes. Experiments were conducted at ambient temperature. Dark controls showed that the models do not thermally degrade under the reaction conditions described.

The sensitized photolysis experiments were performed like those described above, with the inclusion of Rose Bengal (100 μ M) in the solutions and a test tube containing FFA (100–167 μ M) and Rose Bengal photolyzed next to the lignin

model compounds. To purge oxygen from the test tubes, they were fitted with septa and bubbled with argon through Teflon tubing for 30 minutes before photolysis. During photolysis, an argon-flushed syringe was used to remove aliquots. Control experiments showed that FFA did not degrade under these conditions, indicating that oxygen was successfully sparged, as FFA would have reacted with ¹O₂ generated in the system.

HPLC analysis

Lignin model compound and FFA concentrations were measured after photolysis by liquid chromatography using an 1100 Series Hewlett Packard HPLC (Supelco Discovery RP-Amide C16, 150 \times 4.6 mm, 5 μ m particle size column) with 10 μ L injections and a mobile phase containing a mixture of acetonitrile and pH 5 acetate buffered water (10:90 to 40:60) flowing at a rate of 1.0 mL min⁻¹. Absorbance was monitored at 219 nm with a UV-absorbance detector and computer driven data acquisition system (Chemstation).

Quantum yield measurements

The quantum yield of model **7** was determined by irradiating an ethanolic solution of **7** next to an aqueous *p*-nitroanisole-pyridine actinometer solution in quartz test tubes. The quantum yield was determined by using the known quantum yield for *p*-nitroanisole, the absorbances of **7** and *p*-nitroanisole, and the rates for their direct photolysis.²⁴ No correction was made for the different refractive indices of ethanol and water.

Laser flash photolysis

The laser flash photolysis apparatus used in this study is similar to those reported by others.^{25,26} Samples containing lignin model compound (0–50 mM) and ¹O₂ sensitizer (100 μ M perinaphthenone) in EtOH were excited by 4 ns pulses at 355 nm (Nd/YAG, Continuum Minilite II). The interaction of photoexcited perinaphthenone with dissolved oxygen produces ¹O₂, which emits phosphorescence as it relaxes to the triplet state. This phosphorescent decay was monitored by collecting the emitted light through an 1100 nm long-pass filter (CVI Laser Corp.) and a 1271 \pm 18 nm interference filter (CVI Laser Corp.) and focusing it with a collimating lens onto the Ge crystal of a liquid nitrogen cooled ultra-sensitive detector (Model EI-P, Edinburgh Instruments, Ltd.). The detector output was transferred to a digital storage oscilloscope (Tetronix TDS 430A, 400 MHz) where the transient signals were recorded. The transient signals were transferred to a PC workstation for analysis.

Results

Degradation of end-group models under basic conditions:

Reaction with ¹O₂

It was observed that, when deprotonated, the phenolic end-group models do not degrade by direct photolysis under the reaction conditions described (four 175 W Hg-vapor lamps, Pyrex test tubes, 30 minutes). While the deprotonated models are degraded *via* reaction with excited state sensitizer, their reaction with ¹O₂ is much faster (Table 1, Fig. 1). We calculated the rate constant (k_{rxn}) for the reaction of the deprotonated models with ¹O₂ by irradiating them in the presence of a sensitizer and comparing their loss to the loss of a compound degraded under the same conditions, whose k_{rxn} is known (FFA).

To understand the calculation of the rate constant for the reaction of these phenolates with ¹O₂, it is worthwhile to first consider the processes responsible for the formation and loss of ¹O₂ in these experiments (Scheme 1).

We assume that the concentration of ¹O₂ is constant throughout the experiments and apply this steady-state approximation in the development of a kinetic equation that predicts the rate

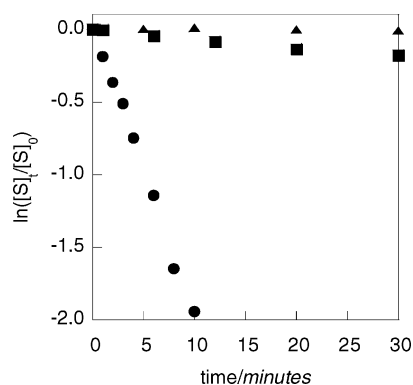
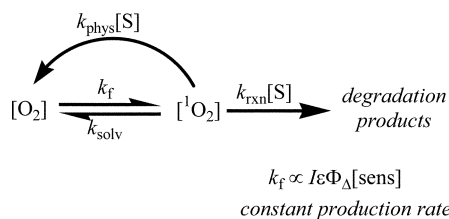


Fig. 1 Logarithmic decay trace for deprotonated dimer **2** in basic EtOH by direct photolysis (▲) and in the presence of Rose Bengal and air (●) and Rose Bengal and argon (■).



Scheme 1 Kinetic model for the formation and loss of $^1\text{O}_2$. O_2 is ground state molecular oxygen, S is substrate, k_f is the zero-order formation rate constant, I is light intensity, ε is the absorption coefficient for the sensitizer, Φ_{Δ} is the quantum yield for $^1\text{O}_2$ ($^1\Delta_g$) formation, and sens is sensitizer. The zero-order $^1\text{O}_2$ formation rate constant, k_f , is proportional to $I\varepsilon\Phi_{\Delta}[\text{sens}]$ and is a function of the depth of the solution and the light screening by other components of the solution. The rate constants k_{solv} , k_{phys} , and k_{rxn} are for deactivation of $^1\text{O}_2$ by solvent, physical quenching by S, and chemical reaction with S, respectively.²⁷

of substrate disappearance due to reaction with $^1\text{O}_2$ [eqn. (1)].

$$-\frac{d[S]}{dt} = \frac{k_f k_{\text{rxn}}[S]}{k_{\text{solv}} + (k_{\text{rxn}} + k_{\text{phys}})[S]} \quad (1)$$

These experiments were conducted in the first-order kinetic regime described by eqn. (2).

$$\frac{-d[S]}{dt} = \frac{k_f k_{\text{rxn}}[S]}{k_{\text{solv}}} \quad \text{when } (k_{\text{rxn}} + k_{\text{phys}})[S] \ll k_{\text{solv}} \quad (2)$$

The models and FFA were photolyzed in the same solvent and side-by-side so that, assuming neither k_f nor k_{solv} vary between samples, the ratio of the observed decay rates for the models and FFA is equal to the ratio of their reaction rate constants. Because k_{rxn} for the reaction of FFA with $^1\text{O}_2$ is known ($1.96 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in EtOH),²⁸ k_{rxn} for the lignin model compounds can be calculated.

The bimolecular rate constants for the reaction of deprotonated phenolic dimers **1–3** range from 2.1 to $2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and do not show a dependence on the number of methoxy substituents on the nonphenolic ring. Similarly, deprotonated monomeric models **4–6** react readily with $^1\text{O}_2$, though a marked dependence on the phenol's methoxy substituents is observed; reaction rate constants range from $0.96 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the unsubstituted model **4** to $7.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for dimethoxy-substituted model **6** (Table 1).

To verify that these reactions occur by reaction with $^1\text{O}_2$, the photolysis of model **2** was conducted in a solution of 79% EtOD in EtOH. Because the lifetime of $^1\text{O}_2$ is approximately doubled in EtOD (30 μs in EtOD compared to 16 μs in EtOH²⁹), an enhancement in the degradation rate is expected in EtOD. It was calculated that reaction with $^1\text{O}_2$ in the 79% EtOD solutions should be 1.6 times faster that observed in EtOH, and the observed enhancement is 1.7.

In contrast to aerated, sensitized photolyses, where the primary loss pathway for phenolates **1–6** is reaction with $^1\text{O}_2$, under argon-sparged conditions, degradation of the end-group phenolates **1–6** occurs *via* reaction with excited state sensitizer. From the plots of $\ln([S]_t/[S]_0)$ versus time, one sees that this reaction is negligible compared to the models' reaction with $^1\text{O}_2$ (Fig. 1).

Degradation of end-group models under neutral conditions: Reaction with excited state sensitizer

Like their deprotonated analogs, models **1–6** do not degrade by direct photolysis under the experimental conditions described. Nor do they react with $^1\text{O}_2$. Dimers **1–3** and monomer **5** are, however, degraded by excited state sensitizer (Fig. 2). For the dimers, the observed rate of degradation by reaction with excited state sensitizer is independent of the phenol's protonation state. While the reaction of deprotonated phenols with excited state sensitizer is considered negligible compared to the reaction of phenolates with $^1\text{O}_2$, the reaction of the lignin model compounds with excited state sensitizer predominates under neutral conditions because the neutral phenols react slowly with $^1\text{O}_2$.

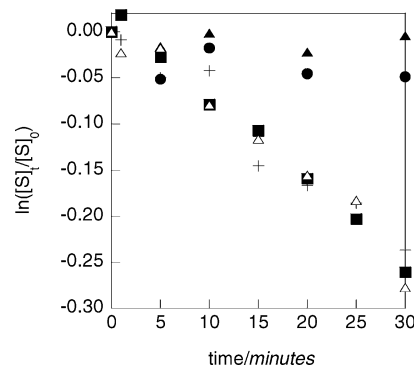


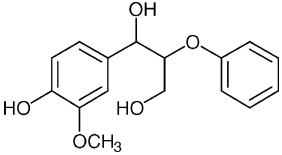
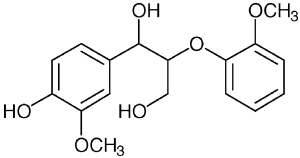
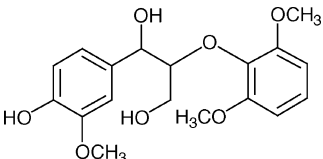
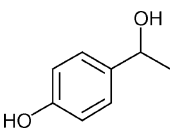
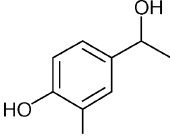
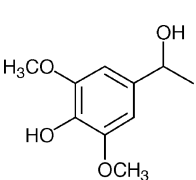
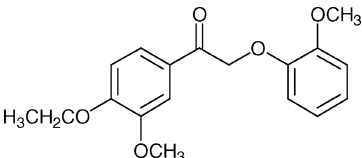
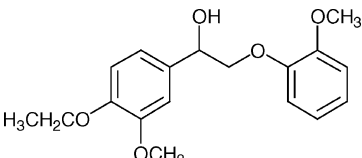
Fig. 2 Logarithmic decay trace for dimer **2** in EtOH by direct photolysis (▲) and in the presence of Rose Bengal and air (●) and Rose Bengal and argon (■). Also, degradation of dimer **1** (+) and dimer **3** (Δ) in the presence of Rose Bengal and argon.

We have developed methods to use laser flash photolysis (LFP) to quantify the interaction (due to quenching or reaction) of lignin model compounds with both excited state sensitizer and $^1\text{O}_2$. The transient $^1\text{O}_2$ signals obtained show that in neutral ethanol, increasing the concentration of lignin model compound effects both the decay portion and the amplitude of the transient signal (see ESI†). The increase in steepness of the decay portion of the transient is due to the physical quenching of $^1\text{O}_2$ by the substrate (k_{phys}) and the reaction of $^1\text{O}_2$ with the substrate (k_{rxn}). We describe the sum of these rate constants as k_{tot} . Because steady-state photolysis shows that reaction of the neutral lignin model compounds with $^1\text{O}_2$ does not occur, the change in the decay portion of the transient signal is due solely to quenching of $^1\text{O}_2$ by substrate ($k_{\text{tot}} \approx k_{\text{phys}} \gg k_{\text{rxn}}$). The decrease in the amplitude of the transient signal is due to the loss of excited state sensitizer due to physical quenching by or chemical reaction with the substrate, because both processes prevent the formation of $^1\text{O}_2$. The rate constant for the sum of these processes is k_T .

We have determined $k_{\text{tot}} (\approx k_{\text{phys}})$ for models **1–6** by exponentially fitting the decay portion of the LFP traces to determine the lifetime of $^1\text{O}_2$ in each solution. The slope of the plot of the observed rate constant, k_{obs} , versus substrate concentration gives k_{tot} (Fig. 3). We determined that k_{tot} for the phenolic end-group models is only slightly larger than the rate constant for the quenching of $^1\text{O}_2$ by ethanol ($7.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) (Table 1, Fig. 3).

Using LFP we quantified the interaction of substrate with excited state sensitizer (k_f) according to Scheme 2. From the kinetic model presented in Scheme 2, an expression relating the

Table 1 Rate constants for the reaction and quenching of lignin model compounds with $^1\text{O}_2$ and excited state sensitizer

Model	Structure	$\text{p}K_a$	Phenolate	Phenol	
			$k_{\text{rxn}}/10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ }^a$	$k_{\text{tot}}/10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ }^b$	$k_{\text{T}}/10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ }^b$
1		10.0	2.4	0.025	16
2		10.1	2.6	0.091	29
3		10.0	2.1	0.11	18
4		9.9	0.96	< 0.0073	5.4
5		9.9	3.5	0.15	26
6		10.1	7.2	0.32	75
7		c	c	c	c
8		c	c	c	c

^a Measured in 90 mM NaOEt in EtOH. ^b Measured in EtOH. ^c Not measured.

area (A) under each transient signal to k_{T} was derived [eqn. (3), see ESI for derivation[†]].

$$\frac{A_0}{A_s} = 1 + \frac{k_{\text{T}}}{k_{\text{O}_2}[\text{O}_2]}[\text{S}] \quad (3)$$

Thus, plotting A_0/A_s versus $[\text{S}]$ yields a straight line with a y intercept of 1 and a slope of $k_{\text{T}}/(k_{\text{O}_2}[\text{O}_2])$. Using published values of $2.33 \times 10^9 \text{ s}^{-1}$ for k_{O_2} ³⁰ and 0.0021 M for $[\text{O}_2]$ at 25 °C,³¹ one can determine k_{T} (Table 1, Fig. 4).

Our calculations show that the dimeric models studied have similar triplet quenching rate constants, ranging from 16 to $29 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Again, the monomers vary significantly in their reactivity, with the unsubstituted model 4 having a k_{T} of $5.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and the dimethoxy substituted model 6 having a k_{T} value of $75 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. With the given experimental procedure it was not possible to determine what fraction of k_{T} is due to reaction with excited state sensitizer and which part is due to quenching of the excited state sensitizer by the lignin model

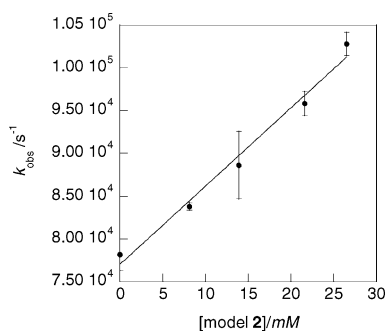
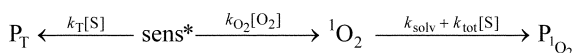


Fig. 3 Plot of observed rate constant for quenching of $^1\text{O}_2$ by model **2** in EtOH versus concentration of model **2**, using perinaphthenone as a sensitizer. Each data point is the average of three experiments and the error bars show one standard deviation ($R^2 = 0.98$).



Scheme 2 Kinetic model for measuring lignin model compound interaction with triplet sensitizer. P_T is the product formed through reaction of S and sens^* where sens^* is excited state sensitizer, $\text{P}_{^1\text{O}_2}$ is the product formed through reaction of S and $^1\text{O}_2$, k_{O_2} is the rate constant for the formation of $^1\text{O}_2$ by 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_{tot} is the sum of k_{phys} and k_{rxn} , which are the rate constants for physical quenching of $^1\text{O}_2$ by S, and chemical reaction of $^1\text{O}_2$ with S, respectively. (See Scheme 1 for descriptions of other variables.)

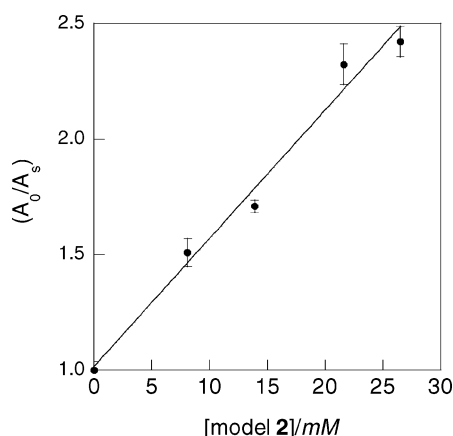


Fig. 4 Plot of A_0/A_s versus concentration of model **2**, where A_0 and A_s is the area under the LFP transient, obtained in EtOH using perinaphthenone as a sensitizer. Each data point is the average of three experiments and the error bars show one standard deviation ($R^2 = 0.98$).

compound, but increasing the number of methoxy substituents on the phenol clearly increases k_T .

Reactivity of inner-core models: Direct photolysis

Inner-core models **7** and **8** showed considerably different reactivity than models **1–6**. While **1–6** were not degraded by direct photolysis, oxidized model **7** was degraded by direct photolysis only, with no additional products formed in the presence of Rose Bengal. The quantum yield of **7** was calculated to be 0.27. Reduced inner-core model **8** was recalcitrant under the conditions used, as it did not degrade by direct photolysis or with $^1\text{O}_2$ or excited state sensitizer (Fig. 5).

Self-sensitized degradation

To assess the ability of lignin to sensitize its own degradation, a representative phenolic model (model **2**) and oxidized inner-core model **7** were irradiated in the same test tube under

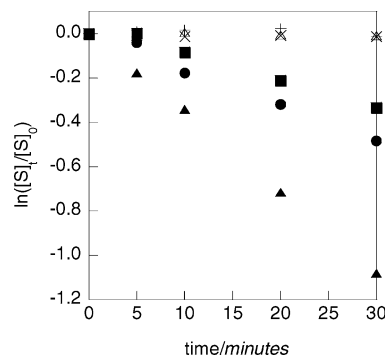


Fig. 5 Logarithmic decay trace for dimers **7** (\blacktriangle) and **8** (\triangle) in EtOH by direct photolysis, dimers **7** (\bullet) and **8** ($+$) in the presence of Rose Bengal and air, and dimers **7** (\blacksquare) and **8** (\times) in the presence of Rose Bengal and argon.

basic conditions. Model **7** acted as a sensitizer, effecting the degradation of **2**. Quantifying the kinetics of this process is difficult because the sensitizer, model **7**, also degrades; a plot of $\ln([S]_t/[S]_0)$ versus time shows that the loss of model **2** slows as the degradation proceeds (Fig. 6).

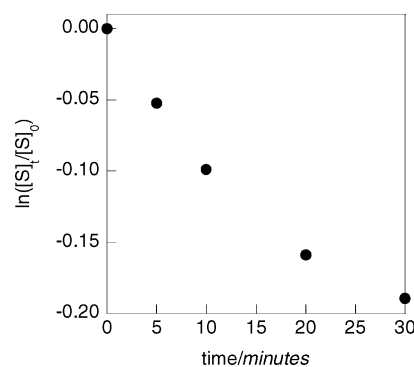


Fig. 6 Logarithmic decay trace for deprotonated dimer **2** in basic EtOH in the presence of oxidized inner-core model **7**.

Discussion

There is a considerable amount of research that has been conducted on the photodegradation of lignin and lignin model compounds like the ones used in this study, but deciphering the role of each of lignin's main functional groups in its photodegradation has not been previously described. To this end, we have assessed the effect of the presence of a phenol functional group and its speciation, because phenols are known for their photochemical reactivity and the formation of quinones is suspected to be a cause of the photoyellowing of paper. We have also assessed the effect of the presence of carbonyl groups in lignin's photodegradation because they are suspected to accelerate cleavage of lignin's $\beta\text{-C-O}$ bonds and may, too, cause paper to photoyellow. Finally, because lignin is often characterized by the number of aryl ring methoxy substituents, understanding how these affect its photodegradation is helpful in better understanding the contribution of different plant sources of lignin to the global carbon cycle.

The enhanced degradation of lignin under sensitized, basic conditions has been observed before, and $^1\text{O}_2$ has been implicated as the species responsible for lignin's fragmentation. For example, the photolysis of lignin derived from corn husks in the presence of hydrogen peroxide proceeds about six times faster under basic conditions than under neutral conditions, and although $^1\text{O}_2$ is believed to be primarily responsible for the lignin's degradation, it is undoubtedly not the only reactive oxygen species (ROS) present.³² Our experiments show

that under basic, sensitized conditions, reaction with $^1\text{O}_2$ is responsible for the degradation of the phenolic models examined and that this reaction proceeds with bimolecular rate constants of 0.96 to $7.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The phenolates also react with excited state sensitizer under oxygen-sparged conditions at rates comparable to those observed in the reaction of neutral phenolic models and excited state sensitizer. Under oxic conditions, we believe that reaction of the phenolate models with $^1\text{O}_2$ dominates reaction with triplet sensitizer. This is based both on literature precedent³³ and on the fact that removal of O_2 causes a dramatic decrease in degradation of the phenolates. While this finding has potential implications for the paper manufacture industry, it has few environmental implications because the $\text{p}K_a$ of each model is sufficiently high such that they exist predominately in their neutral form in the natural environment.

Analysis of our kinetic data provides several clues that this reaction occurs at the phenolic ring. First, the degradation of the phenolic models only occurs when the phenol is deprotonated (and therefore more electron-rich than its neutral analog). Second, the rate of degradation of the dimeric phenolates **1**–**3** does not show a dependence on the addition of electron donating methoxy substituents on the nonphenolic ring, as would be expected if the nonphenolic ring was the reaction site. There is, however, a variation in k_{rxn} values for the monomeric phenolates **4**–**6**, and this variation follows the trend expected, with k_{rxn} increasing with the addition of electron-donating methoxy substituents.

Based on our studies on the degradation of the neutral phenols under sensitized, aerated conditions (where degradation is not observed) and under sensitized, argon-sparged conditions (where degradation is observed), we believe that others¹³ have misattributed the sensitized degradation of neutral models **2** and **3** to reaction with $^1\text{O}_2$, and that the main degradation mechanism of these and other neutral phenolic models is actually reaction with excited state sensitizer.

The reaction of phenols with excited state sensitizer is predated. For example, the porphyrin-sensitized photooxidation of 4-chlorophenol yields *p*-benzoquinone and *p*-hydroquinone in the presence of O_2 and only *p*-hydroquinone in the absence of O_2 . The formation of *p*-benzoquinone is attributed to the substrate's reaction with $^1\text{O}_2$, and the formation of *p*-hydroquinone is attributed to the reaction of 4-chlorophenol with excited state sensitizer.³⁴ The literature on the degradation of lignin sensitized by triplet sensitizers is sparse compared to the literature on lignin's degradation by ROS, but as Frimmel *et al.* suggested in 1987 when discussing the effect of humics on the photochemical reactions that take place in natural waters, "... $^1\text{O}_2$ production is only one possibility for the reaction pathway and may play even a minor role compared to the direct transfer of energy to other reactants."³⁵ Cooper *et al.* add that charge transfer and photoincorporation are possible reaction pathways.³⁶ Laboratory studies on the photolysis of various methoxyphenols in the presence of well-defined sensitizers such as benzophenone, 3'-methoxyacetophenone, and 2-acetonaphthone in water has led some to believe that this reaction occurs *via* electron transfer from the phenol to the sensitizer.¹⁷

As with the reaction of the phenolate models with $^1\text{O}_2$, we have evidence that the interaction between the neutral phenolic models and excited state sensitizer occurs at the phenol ring. Clearly, the methoxy substituents on the phenol affect k_T far more than the methoxy groups on the nonphenolic ring, as the measured k_T values for **1**, **2**, and **3** are similar, and k_T increases with the increasing number of methoxy substituents on the monomer models. We are cautious in this ascription, because k_T is the sum of the rate constants for the quenching of excited state sensitizer and reaction with excited state sensitizer. Based on the trend our k_T values follow, however, and the proposed electron transfer mechanism for this reaction in polar, protic solvents, we propose that the excited state sensitizer and lignin model compound are reacting at the phenol ring. Additional evidence

is provided by kinetic decay plots for the sensitized, non-aerated irradiations of the dimeric models, which have the same slope, showing that they do not vary in their reactivity with excited state sensitizer. Unfortunately, an analogous comparison showing the monomers' varying reactivities is not possible because the logarithmic decay plots for the monomers are nonlinear under the experimental conditions described.

Our hypothesis that the phenolic moiety is the reactive portion of the models is supported by studies on the degradation of lignin in natural waters. It has been observed that, in the summer, the ratio of syringyl to guaiacyl units in lignin decreases with increased salinity in estuaries, indicating lignin's syringyl moieties are preferentially photodegraded as the terrigenous carbon moves from freshwater systems to the ocean.⁵ A related study considered the possibility of variations in lignin's structure as a function of molecular weight and studied the degradation of lignin's high and low molecular weight components separately, finding that in the high molecular weight component, specifically, the syringyl unit is preferentially degraded. The opposite trend is observed in low molecular weight fragments, but this is partially attributed to the conversion of high molecular weight fragments to low molecular weight fragments.³⁷ Yet another study where filtered ocean water was irradiated with natural sunlight for four days showed not only that the ratio of syringyl to guaiacyl rings decreased, but that the ratio of guaiacyl to cinnamyl rings decreased, too, which is consistent with our kinetic analyses.⁶

The degradation of the inner-core model **7** and a similar compound, where a methyl group is substituted for the ethyl group that protects the phenol, have been studied extensively. Our experiments clearly show that the carbonyl group of model **7** is responsible for its degradation, because reduced model **8** does not degrade by direct photolysis. The direct photochemical degradation of **7** and its methyl protected analog has been observed before, and, based on product analysis studies, has been hypothesized to proceed *via* excitation of the carbonyl to a triplet state followed by formation of primary ketyl radicals and cleavage of the $\beta\text{-C-O}$ bond.^{38–40} It has been suspected, however, that this degradation is mediated by $^1\text{O}_2$.^{13,14} We found that, although model **7** is degraded in the presence of Rose Bengal, the reaction is slower in its presence, and we suspect that this may be due to the screening of light by Rose Bengal. To quantify the direct photolysis of model **7**, we determined its quantum yield. The value we calculated (0.27) is close to that of its methyl protected analog (0.32 ± 0.08).⁴¹

To summarize our findings on lignin's photochemical reactivity in natural waters relative to its structure, we believe that the lignin oligomers most resistant to photodegradation are those that lack α -carbonyl and phenolic functionalities. Of the oligomers that are phenolic, the non-methoxy-substituted phenols are more refractory than the methoxy-substituted phenols.

Perhaps one of the most interesting findings in this set of experiments is the concrete evidence we have provided that shows that oxidized model **7** can sensitize the degradation of deprotonated model **2**. This finding supplements a previous experiment that has shown that acetovanillone sensitizes the degradation of an α -reduced phenolic model (1-hydroxy-1-(4-hydroxy-3-methoxy)-2,2-dimethyl propane).^{42,43} In this study, $^1\text{O}_2$ was proposed as an oxidant generated by acetovanillone, but the rate suppression expected upon the addition of $^1\text{O}_2$ quenchers was not always observed, leaving open the possibility of additional reactions taking place, like that of the model with excited state sensitizer itself. In fact, a different study showed that the degradation of the same model was sensitized by a similar ketone (*p*-methoxypropiophenone) under both aerated and oxygen-free conditions.^{44,45} Elucidating the mechanism of the lignin-sensitized photodegradation of lignin is surely an important part of understanding the degradation of aquatic carbon and it warrants further research.

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References

- 1 J. I. Hedges, R. G. Keil and R. Benner, What happens to terrestrial organic matter in the ocean?, *Org. Geochem.*, 1997, **27**, 195–212.
- 2 E. T. Gjessing, *Physical and Chemical Characteristics of Aquatic Humus*, Ann Arbor Science, Ann Arbor, MI, 1976, p. 120.
- 3 S. Opsahl and R. Benner, Distribution and cycling of terrigenous dissolved organic matter in the ocean, *Nature (London)*, 1997, **386**, 480–482.
- 4 R. Benner and B. Biddanda, Photochemical transformations of surface and deep marine dissolved organic matter: Effects on bacterial growth, *Limnol. Oceanogr.*, 1998, **43**, 1373–1378.
- 5 R. Benner and S. Opsahl, Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume, *Org. Geochem.*, 2001, **32**, 597–611.
- 6 S. Opsahl and R. Benner, Photochemical reactivity of dissolved lignin in river and ocean waters, *Limnol. Oceanogr.*, 1998, **43**, 1297–1304.
- 7 O. Lanzalunga and M. Bietti, Photo- and radiation chemical induced degradation of lignin model compounds, *J. Photochem. Photobiol., B*, 2000, **56**, 85–108.
- 8 C. Bonini, M. D'Auria, L. D'Alessio, G. Mauriello, D. Tofani, D. Viggiano and F. Zimbardi, Singlet oxygen degradation of lignin, *J. Photochem. Photobiol., A*, 1998, **113**, 119–124.
- 9 C. Bonini, M. D'Auria, G. Mauriello, D. Viggiano and F. Zimbardi, Singlet oxygen degradation of lignin in the pulp, *J. Photochem. Photobiol., A*, 1998, **118**, 107–110.
- 10 G. Bentivenga, C. Bonini, M. D'Auria and A. De Bona, Singlet oxygen degradation of lignin: a GC-MS study on the residual products of the singlet oxygen degradation of a steam exploded lignin from beech, *J. Photochem. Photobiol., A*, 1999, **128**, 139–143.
- 11 G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona and G. Mauriello, Fine chemicals from singlet-oxygen-mediated degradation of lignin—a GC/MS study at different irradiation times on a steam-exploded lignin, *J. Photochem. Photobiol., A*, 2000, **135**, 203–206.
- 12 C. Bonini, A. Carbone and M. D'Auria, Singlet oxygen mediated degradation of lignin—a kinetic study, *Photochem. Photobiol. Sci.*, 2002, **1**, 407–411.
- 13 C. Crestini and M. D'Auria, Photodegradation of lignin: the role of singlet oxygen, *J. Photochem. Photobiol., A*, 1996, **101**, 69–73.
- 14 C. Crestini and M. D'Auria, Singlet oxygen in the photodegradation of lignin models, *Tetrahedron*, 1997, **53**, 7877–7888.
- 15 G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona and G. Mauriello, Singlet oxygen mediated degradation of Klason lignin, *Chemosphere*, 1999, **39**, 2409–2417.
- 16 S. Canonica, U. Jans, K. Stemmler and J. Hoigne, Transformation kinetics of phenols in water: Photosensitization by dissolved natural organic material and aromatic ketones, *Environ. Sci. Technol.*, 1995, **29**, 1822–1831.
- 17 S. Canonica, B. Hellrung and J. Wirz, Oxidation of phenols by triplet aromatic ketones in aqueous solution, *J. Phys. Chem., A*, 2000, **104**, 1226–1232.
- 18 S. Canonica and M. Freiburghaus, Electron-rich phenols for probing the photochemical reactivity of freshwaters, *Environ. Sci. Technol.*, 2001, **35**, 690–695.
- 19 R. H. J. Creighton and H. Hibbert, Lignin and related compounds. LXXVI. Alkaline nitrobenzene oxidation of corn stalks. Isolation of *p*-hydroxybenzaldehyde, *J. Am. Chem. Soc.*, 1944, **66**, 37–38.
- 20 R. H. J. Creighton, R. D. Gibbs and H. Hibbert, Lignin and related compounds. LXXV. Alkaline nitrobenzene oxidation of plant materials and application to taxonomic classification, *J. Am. Chem. Soc.*, 1944, **66**, 32–37.
- 21 S. Kawai, K. Okita, K. Sugishita, A. Tanaka and H. Ohashi, Simple method for synthesizing phenolic β -O-4 dilignols, *J. Wood Sci.*, 1999, **45**, 440–443.
- 22 J. Sipilä and K. Syrjänen, Synthesis and ^{13}C NMR spectroscopic characterization of six dimeric arylglycerol- β -aryl ether model compounds representative of syringyl and *p*-hydroxyphenyl structures in lignins. On the aldol reaction in β -ether preparation, *Holzforschung*, 1995, **49**, 325–331.
- 23 S. Besombes, D. Robert, J.-P. Utille, F. R. Tavel and K. Mazeau, Molecular modeling of syringyl and *p*-hydroxyphenyl β -O-4 dimers. Comparative study of the computed and experimental conformational properties of lignin β -O-4 model compounds, *J. Agric. Food Chem.*, 2003, **51**, 34–42.
- 24 A. Leifer, *The kinetics of environmental aquatic photochemistry: Theory and practice*, American Chemical Society, Washington, DC, 1988, 304 pp.
- 25 S. Nonell, S. E. Braslavsky and K. Schaffner, Quantum yield of production of singlet molecular oxygen ($^1\Delta_g$) in aqueous dispersions of small unilamellar lipid vesicles. A time-resolved near-IR phosphorescence study, *Photochem. Photobiol.*, 1990, **51**, 551–556.
- 26 S. Nonell and S. E. Braslavsky, Time-resolved singlet oxygen detection, *Methods Enzymol.*, 2000, **319**, 37–49.
- 27 D. E. Latch, B. L. Stender, J. L. Packer, W. A. Arnold and K. McNeill, Photochemical fate of pharmaceuticals in the environment: Cimetidine and ranitidine, *Environ. Sci. Technol.*, 2003, **37**, 3342–3350.
- 28 B. Stender, *The development of a time-resolved singlet oxygen phosphorescence detection system and the quenching of singlet oxygen by pharmaceuticals and personal care products*, MS Thesis, University of Minnesota, Minneapolis, 2001, 100 pp.
- 29 F. Wilkinson, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1995, **24**, 663–1021.
- 30 C. Schweitzer, Z. Mehrdad, A. Noll, E.-W. Grabner and R. Schmidt, Mechanism of photosensitized generation of singlet oxygen during oxygen quenching of triplet states and the general dependence of the rate constants and efficiencies of $\text{O}_2(^1\Sigma_g^+)$, $\text{O}_2(^1\Delta_g)$ and $\text{O}_2(^3\Sigma_g^-)$ formation on sensitizer triplet state energy and oxidation potential, *J. Phys. Chem. A*, 2003, **107**, 2192–2198.
- 31 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 2nd edn., 1993, 420 pp.
- 32 A. E. H. Machado, R. Ruggiero and M. G. Neumann, The photodegradation of lignins in the presence of hydrogen peroxide, *J. Photochem. Photobiol., A*, 1994, **81**, 107–115.
- 33 P. G. Tratnyek and J. Hoigne, Oxidation of substituted phenols in the environment: A QSAR analysis of rate constants for reaction with singlet oxygen, *Environ. Sci. Technol.*, 1991, **25**, 1596–1604.
- 34 E. Silva, M. M. Pereira, H. D. Burrows, M. E. Azenha, M. Sarakha and M. Bolte, Photooxidation of 4-chlorophenol sensitised by iron meso-tetrakis(2,6-dichloro-3-sulphophenyl)porphyrin in aqueous solution, *Photochem. Photobiol. Sci.*, 2004, **3**, 200–204.
- 35 F. H. Frimmel, H. Bauer, J. Putzien, P. Murasecco and A. M. Braun, Laser flash photolysis of dissolved aquatic humic material and the sensitized production of singlet oxygen, *Environ. Sci. Technol.*, 1987, **21**, 541–545.
- 36 W. J. Cooper, R. G. Zika, R. G. Petasne and A. M. Fischer, *Sunlight-induced photochemistry of humic substances in natural waters: Major reactive species*, ed. I. H. Suffet and P. MacCarthy, American Chemical Society, Washington, DC, 1989, pp. 333–362.
- 37 P. J. Hernes and R. Benner, Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments, *J. Geophys. Res. [Oceans]*, 2003, **108**, 7/1–7/9.
- 38 C. Vanucci, P. Fournier de Violette, H. Bouas-Laurent and A. Castellán, Photodegradation of lignin: A photophysical and photochemical study of a nonphenolic α -carbonyl β -O-4 lignin model dimer, 3,4-dimethoxy- α -(2'-methoxyphenoxy)acetophenone, *J. Photochem. Photobiol., A*, 1988, **41**, 251–265.
- 39 B. J. Zhao, M. C. Depew, N. A. Weir and J. K. S. Wan, Some mechanistic aspects of the light-induced yellowing of lignin: A further study of the photochemical reactions of α -guaiacyloxy- β -hydroxypropioveratrone and some substituted methoxybenzenes, *Res. Chem. Intermed.*, 1993, **19**, 449–461.
- 40 D. S. Argyropoulos and Y. Sun, Photochemically induced solid-state degradation, condensation and rearrangement reactions in lignin model compounds and milled wood lignin, *Photochem. Photobiol.*, 1996, **64**, 510–517.
- 41 J. A. Schmidt, A. B. Berinstain, F. De Rege, C. Heitner, L. J. Johnston and J. C. Scaiano, Photodegradation of the lignin model α -guaiacyloxyacetoveratrone: Unusual effects of solvent, oxygen and singlet-state participation, *Can. J. Chem.*, 1991, **69**, 104–107.
- 42 I. Forsskahl, Aspects of photosensitized lignin oxygenation, *J. Photochem.*, 1984, **25**, 197–209.
- 43 I. Forsskahl, Product analysis of the photo-oxygenation of *tert*-butylguaiacylcarbinol sensitized by 4-hydroxy-3-methoxy acetophenone, *J. Photochem.*, 1984, **27**, 363–374.
- 44 I. Forsskahl, H. Tylli and C. Olkkonen, An experimental and computer modeling study of the photochemical reaction of *tert*-butylguaiacylcarbinol sensitized by *p*-methoxypropiofenone in aerated dimethoxyethane solution, *J. Photochem. Photobiol., A*, 1990, **50**, 407–423.
- 45 I. Forsskahl and H. Tylli, Experimental and computer modeling study of the photochemical reactions of *tert*-butylguaiacylcarbinol sensitized by *p*-methoxypropiofenone in oxygen-free dimethoxyethane, *J. Photochem.*, 1984, **27**, 85–99.