Photochemical Production of Carbon Monoxide from Dissolved Organic Matter: Role of Lignin Methoxyarene Functional Groups

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ABSTRACT: Carbon monoxide (CO) is the second most abundant identified product of dissolved organic matter (DOM) photodegradation after CO$_2$, but its formation mechanism remains unknown. Previous work showed that aqueous photodegradation of methoxy-substituted aromatics (ArOCH$_3$) produces CO considerably more efficiently than aromatic carbyls. Following on this precedent, we propose that the methoxy aromatic groups of lignin act as the C source for the photochemical formation of CO from terrestrial DOM via a two-step pathway: formal hydrolytic demethylation to methanol and methanol oxidation to CO. To test the reasonableness of this mechanism, we investigated the photochemistry of eight lignin model compounds. We first observed that initial CO production rates are positively correlated with initial substrate degradation rates only for models containing at least one ArOCH$_3$ group, regardless of other structural features. We then confirmed that all ArOCH$_3$-containing substrates undergo formal hydrolytic demethylation by detecting methanol and the corresponding phenolic transformation products. Finally, we showed that hydroxyl radicals, likely oxidants to initiate methanol oxidation to CO, form during irradiation of all models. This work proposes an explicit mechanism linking ubiquitous, abundant, and easily quantifiable DOM transformation products. Our results further hint that methanol may be an abundant (yet overlooked) DOM photoproduction and a likely precursor of formaldehyde, formic acid, and CO$_2$ and that lignin photodegradation may represent a source of hydroxyl radicals.

KEYWORDS: dissolved organic matter photodegradation, carbon monoxide, reaction mechanism, lignin, methanol, hydroxyl radicals, carbon cycling, methoxy-substituted aromatics

INTRODUCTION

Carbon monoxide (CO) is a trace gas that plays an important role in modulating hydroxyl radical (OH$^*$) concentrations in the troposphere, therefore influencing the residence time of greenhouse gases such as methane and halocarbons.$^{1-5}$ Among other sources, CO can be produced from the photodegradation of dissolved organic matter (DOM). Albeit contributing only a minimal fraction of the global CO budget,$^1$ photochemical production from DOM photolysis is relevant in remote ocean regions or in environments characterized by significant inputs of terrestrial DOM.$^{6-8}$ CO is also involved in the production of carbonyl sulfide (OCS) from DOM photolysis.$^6$ Photochemical processes are significant players in the global OCS budget, but their contributions are not yet well constrained.$^9-16$ An improved understanding of OCS sources and sinks can indirectly contribute to better climate simulations, as this gas is used as a tracer of gross primary productivity.$^9,11$ In addition, CO has been used as a proxy for the photoproduction of CO$_2$, CH$_4$, and biolabile organic carbon$^{5,12-16}$ (even though this approach proved to be inaccurate for CO$_2$)$^{5,17,18}$ and for developing models of mixed layer processes.$^5,19,20$

Despite the interest in CO biogeochemistry, little is currently known about its photochemical formation mechanism. Redden$^{21}$ hypothesized that acetone, acetaldehyde, and other carbonyl-containing DOM photoproducts might undergo Norrish type I fragmentation and release CO. Others proposed that photosensitized degradation of $\alpha$-ketoacids (e.g., pyruvic acid) may produce acetyl radicals, which then fragment to CO.$^6$ Even if these processes are well-established in traditional photochemistry,$^{22-27}$ low environmental concentrations and yields limit the role of low-molecular-weight carbonyls as CO precursors in natural environments.$^5,21$
Furthermore, Stubbins et al. observed up to 300 times higher CO production from photolysis of ethoxy- and methoxy-substituted phenols compared to aromatic carbonyls. This finding reinforces the idea that carbonyls in general, not only low-molecular-weight ones, are secondary CO precursors and hints at an alternative production mechanism.

Following on the results reported by Stubbins et al., we propose that lignin is an environmentally relevant precursor of CO. Lignin is the second most abundant biopolymer on Earth after cellulose, consisting of three aromatic core units [p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)] connected mostly via β-O-4 linkages (Figure 1). G and S functionalities, which together account for 65 to 95% of the total core units across all plant types, contain one and two aromatic methoxy groups (ArOCH₃), respectively. Lignin is a major component of terrestrial DOM and also comprises a small portion of marine DOM, making it a quantitatively relevant source of methoxy aromatics in aquatic ecosystems.

We hypothesize that lignin’s aromatic methoxy groups act as the C source for the formation of CO via a two-step mechanism: conversion of the aromatic methoxy group to methanol via direct photolysis; and methanol oxidation to CO via indirect photolysis (Figure 1). Two sets of observations justify this hypothesis. Several authors reported evidence of ArOCH₃ and Ar-OCH₃ cleavage of lignin model compounds, with consequent formation of methane, ethane, and chloroform (ArOCH₃ cleavage) or methanol (Ar-OCH₃ cleavage). In particular, Dallin et al. showed that direct photolysis of syringic acid in D₂O produced methanol (CH₂OH) via singlet excited state protonation followed by nucleophilic attack by water (eq 1).

\[
\text{H}_2\text{CO}_3^- + \text{H}_2\text{O} \xrightarrow{hv} \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3^- + \text{H}_3\text{O}^+ \\
\text{H}_2\text{CO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{H}_2\text{O}
\]

In the presence of OH⁺ or other reactive species, methanol can further oxidize to CO, as it has been observed in several systems. Our hypothesis that lignin is an important source of CO also agrees with the following observations: Apparent quantum yields for CO production are higher in freshwater compared to seawater (Mopper et al. and refs therein); both CO yields and lignin DOM content generally decrease along a salinity gradient, CO photo-production rates and quantum yields are correlated with DOM aromaticity and the specific ultraviolet absorbance at 254 nm, respectively (even though this correlation is weak for large marine-based data sets); and, photodegradation of dead plant leaves can release CO. Finally, several authors reported loss of methoxy groups during photodegradation of lignin from different sources (Paulsson and Parkás and refs therein).

To evaluate the viability of this pathway, we investigated the photochemistry of eight lignin model compounds (Figure 2A) focusing on specific precursors and products. We first established structure-reactivity relationships between photochemical reactivity and CO production. We further sought evidence for the formation of methanol and aromatic 3-hydroxy groups via ¹H NMR spectroscopy and mass spectrometry (MS), respectively. Finally, we quantified OH⁺ to confirm that indirect photodestruction of methanol can occur under our experimental conditions. To the authors’ knowledge, this work is the first to propose an explicit mechanism for the formation of CO from the photodegradation of terrestrial DOM. We also unambiguously identified methanol as an abundant photoproduction of lignin model compounds and as a potential precursor of other ubiquitous C₃ photoproducts, and we showed that photodestruction of lignin model compounds can be a source of OH⁺. Future work using natural lignin and more representative solution compositions will be needed to confirm the environmental relevance of these processes.

### MATERIALS AND METHODS

#### Chemicals

Chemicals were purchased from commercial vendors (Text S1) or synthesized via modified literature procedures (Text S2, Figure S1). Experimental solutions were obtained upon dilution of concentrated stocks in nanopure water (Text S1). At the experimental pH (5.8–6.5), all phenols were present in their protonated form (≥97%, Text S3).

#### Photolysis Experiments

We conducted all photochemistry experiments inside a photochemical reactor (Southern New England Ultraviolet Company, USA) equipped with a fan, a motorized turntable, and UV bulbs (Southern New England Ultraviolet Co., RPR 3000A; Figure 2B). Most experiments were conducted with 6 lamps; in selected cases (specified in the text), we used 12 bulbs to accelerate photocatalytic rates. When using 6 lamps, the solution temperature was approximately 29–31 °C.

To quantify CO, we irradiated aqueous solutions of each model compound (50 µM) in headspace-free borosilicate test tubes (Pyrex, 15 × 85 mm; disposable) capped with rubber septa (Text S4.1). At each time point, one test tube was removed from the carousel and replaced with a water-filled tube. At the end of the irradiation, ≈6 mL of each solution was transferred into an nitrogen-flushed 20-mL serum vial for headspace gas chromatography (GC) measurements (Text...
S4.2); the leftover volume (150 µL) was analyzed via ultrahigh-performance liquid chromatography (UPLC).

In $^1$H NMR experiments, we irradiated solutions containing 0.8–1.1 mM of a substrate and 0.48 mM of methanesulfonate (internal standard) in D$_2$O in an NMR tube. Every 30 min, each tube was shaken vigorously to assure mixing (Text S5, Figure S2A). At selected time points, we removed the tube from the photoreactor, collected a $^1$H NMR spectrum, and then continued the irradiation. At the beginning and end of each experiment, we collected an aliquot (in triplicate), diluted it 20- or 40-fold, and quantified the substrate concentration via UPLC.

For MS measurements, we employed borosilicate test tubes containing aqueous solutions of each model compound (50 µM; 12 lamps). At each time point, we collected aliquots for UPLC (150 µL) and MS (800 µL) analyses. To quantify [OH$^+$]$_w$, we used the same setup (with 6 lamps), but experimental solutions contained benzoate (BA$_w$ 10 µM or 1 mM) in addition to the model compound.$^{53,54}$ Unlike experiments for CO quantification, the borosilicate test tubes were left uncapped.

All experiments were performed at least in duplicate, except for $^1$H NMR and MS, which we carried out as single measurements. Controls confirmed that chemical changes were solely due to photochemical processes (Text S6, Figures S3 and S4).

**Sample and Data Analysis. Lignin Model Compounds.** Lignin model compounds were analyzed by UPLC (Waters ACQUITY) with a C18 column (Acquity, BEH130 C18, 1.7 µm; 2.1 x 150 mm) and a photodiode array detector. Analyses were performed in isocratic mode using different combinations of aqueous and organic eluents, 5 µL injection volume, and flow rates of 0.15–0.20 mL min$^{-1}$. Details for each compound are given in Table S1.

In CO production experiments, data from at least duplicate experiments were pooled together and fitted to eq 2 (Matlab R2018b), where $k_{obs}$ (h$^{-1}$) is the pseudo-first-order photodegradation rate constant of substrate A.

$$\frac{[A]_t}{[A]_0} = e^{-k_{obs}t}$$

(2)

The initial parent compound degradation rate was calculated as $k_{parent} = k_{obs}[A]_0$ where $[A]_0$ was measured via UPLC.

**Carbon Monoxide.** Headspace CO concentrations in the serum vials ($p_{CO,hs}$) were quantified via GC analyses as described in Borduas-Dedekind et al.$^{55}$ (Text S7.1) and were then converted to aqueous-phase CO concentrations ([CO]$_a$ in µM) in the headspace-free test tubes used for irradiation via eq 3.

$$[CO]_a = \frac{p_{CO,hs} V_{hs}}{RT V_{eq}} \left( \frac{1}{K_{CO}} \right)$$

(3)

where $p_{CO,hs}$ is the headspace serum vial concentration converted in atm, $R$ is the gas constant, $T$ is the air temperature, $V_{hs}$ is the headspace volume in the serum vial, $V_{eq}$ is the volume of liquid in the same vial, and $K_{CO}$ is the temperature-dependent Henry’s Law constant for CO.$^{56}$ Details are given in Text S7.2. For each compound, we calculated the CO conversion efficiency after 6 h of irradiation ($Y_{CO}$) via eq 4.

$$Y_{CO} = \frac{[CO]_{hs,corr}}{[A]_0 - [A]_hs}$$

(4)

where $[CO]_{hs,corr} = [CO]_hs - [CO]_0 - [CO]_{blank}$ is the amount of photoproduced CO corrected for time zero ($[CO]_0 = 0–0.20$ µM) and blank contributions ($[CO]_{blank} = 1.25–2.62$ µM, depending on the number of lamps), while $[A]_0$ and $[A]_hs$ are initial and final substrate concentrations quantified via UPLC, respectively. Blank contributions are caused by photodegradation of organic carbon leached from the rubber stoppers (Text S7.3, Figure S5). In addition to $Y_{CO}$, we fitted the CO production kinetics to obtain the initial CO production rate as $R_{CO}^0 = ab[A]_0$, where $a$ and $b$ are the fitting parameters of eq 5. $[A]_0$ is the initial substrate concentration obtained via UPLC, and [CO], is the total CO produced during irradiation.

$$\frac{[CO]_0}{[A]_0} = a(1 - e^{-bt})$$

(5)

For a few compounds, we fitted the CO kinetics with a linear model because the exponential fit did not converge; in this case, we obtained $R_{CO}^0$ from the slope of the linear regression line.

**Methanol.** We performed $^1$H NMR analyses on a Bruker AVANCE III-400 spectrometer using D$_2$O as the solvent and methanesulfonate (2.81 ppm) as the internal standard. Each
Liquid Chromatography Coupled to High-Resolution MS. Samples were injected (50 μL) at a flow rate of 0.3 mL min⁻¹ into a LC system (UltiMate 3000 UHPLC system, Dionex) equipped with a C18 column (3 μm particle size, 3 × 150 mm, Atlantis) at 30 °C. Analyses were performed using the following gradient (A = 0.1% formic acid in ultrapure water; B = 0.1% formic acid in methanol): 0–1 min, A:B = 95:5; 1–17 min, from 95:5 to 5:95; 17–25 min, 5:95; 25–27 min, from 5:95 to 95:5; 27–30 min, 95:5. The LC was coupled to a quadrupole-Orbitrap mass spectrometer (Thermo Scientific, Bremen) operated with an electrospray ionization source in positive (4 kV spray voltage, 250 °C capillary temperature, 40 sheath gas flow rate, 10 auxiliary gas flow rate) or negative mode (GD2 only; 3 kV spray voltage, 325 °C capillary temperature, 40 sheath gas flow rate, 10 auxiliary gas flow rate). Data were acquired in full scan mode with m/z range 100–1000 at 140,000 resolution (at 200 m/z). MS² data were obtained with a top-5 experiment with normalized collision energy of 30 at 17,500 resolution (at 200 m/z).

We used Compound Discoverer 3.2 (CD 3.2, Thermo Scientific, Germany) to identify features generated during irradiation and to assign molecular formulas. A list of expected masses and chemical structures of transformation products (TPs) was included in the data analysis workflow in CD3.2. For each molecular formula, we confirmed that its peak area was absent before irradiation, was at least 5 times higher in irradiated samples compared to the blank, and showed growing or growth-and-decay patterns in peak area as a function of time. Using Freestyle (Thermo Scientific, Germany), we extracted peak areas, total ion chromatograms, MS, and MS² spectra of the main TPs. We then compared MS² fragmentation patterns to in silico predictions obtained with MetFrag, as TPs library spectra were not available. This information was used to assess the level of confidence according to Schymanski et al.

Hydroxyl Radicals (OH*). BA was quantified via UPLC (Table S1). Its pseudo-first-order degradation rate constant \( k_{\text{abs,BA}} \) obtained from the slope of a ln([BA]/[BA]₀) vs time plot was employed to calculate [OH*]ₜₐ as per eq 7.

\[
[\text{OH}^*]_\text{t}_\text{a} = \frac{k_{\text{abs,BA}}}{k_{R,\text{BA},\text{OH}-}} \times \frac{[\text{BA}]}{[\text{BA}]_0} \tag{7}
\]

where \( k_{R,\text{OH}-} = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) is the second-order rate constant for the reaction of OH* with BA. For compounds not inducing BA decay, [OH*]ₜₐ was estimated from the ratio of their p-hydroxybenzoic acid production rate \( R_{\text{PHBA}} \) to that of GD1, that is, [OH*]ₜₐ \( \approx \frac{R_{\text{PHBA}}}{R_{\text{PHBA}} \cdot [\text{OH}^*]_\text{GD1}} \).

Other Instrumental Analyses. UV–vis measurements were performed with a Varian 100 Bio spectrometer and a 1-cm pathlength quartz cuvette. The instrument was run in double beam mode using nanopure water as the blank.

### RESULTS

Description of the Lignin Model Compounds. The selected model compounds reproduce several aspects of lignin chemistry, namely, the substitution pattern of the aromatic core unit (H, G, or S), the oxidation state of the α-carbon (α-alcohol or α-ketone), and the presence of ancillary groups (Figure 2A). Based on the proposed mechanism, we expected the presence or absence of methoxy groups to be the most relevant variable controlling photochemical CO production. Specifically, guaiacyl (G1, G2, GD1, and GD2) and syringyl (S1 and S2) models are expected to produce CO, while the p-hydroxyphenyl derivatives (H1 and H2) are not. The effect of the α-carbon oxidation state was less clear prior to the study. We anticipated methoxy-substituted ketones to be more photo reactive than the corresponding alcohols in the 290–400 nm range due to the n → π* carbonyl absorption band, but we could not anticipate how this fact would impact CO production.

Correlation between Chemical Structure and CO Production. To assess the plausibility of the proposed mechanism, we first established qualitative and quantitative correlations between molecular structure and CO photoproduction. To this aim, we irradiated an aqueous solution of each model compound using a headspace-free setup designed to limit CO partitioning to the gas phase. We then quantified substrate loss and CO production via liquid chromatography with UV detection and headspace GC, respectively.

All compounds with at least one aromatic methoxy group produced CO after 6 h of UV irradiation, with CO conversion efficiencies (Y_CO) ranging from 10.2 to 17.6% (Table 1; Y_CO is defined as moles of CO produced per mole of substrate degraded, eq 4). Comparison between Y_CO values of G (11.5–17.6%) and S models (10.2–11.2%) suggests that the presence of at least one ArOCH₃ group, not the number of such functionalities, is the most relevant CO predictor. All guaiacyl α-alcohols have comparable Y_CO values (11.5–14.4%), hinting that ancillary groups do not considerably influence CO photoproduction in this class of compounds.

The α-ketone H2 also produced CO (2.2%), albeit with lower efficiency compared to methoxy-substituted compounds (≥10.2%). This result indicates that a secondary CO production pathway, perhaps a Norrish type I reaction, may be operative during UV irradiation of this molecule. Along the same lines, the α-ketone G2 had slightly higher Y_CO (17.6%) compared to the corresponding α-alcohol G1 (∼12%); however, this difference was negligible for S compounds. We highlight that the comparable Y_CO values of alcohols and ketones with the same substitution pattern is a strong indication that the α-carbonyl is not involved in the primary CO production pathway. This conclusion also agrees with Stubbins et al., who showed that aromatic ketones lacking ArOCH₃ groups are not efficient CO precursors. Trace amounts of CO were also detected during UV irradiation of H1 but controls indicated that ≥85% of the gas originated from the photodegradation of the organic carbon leached from the stoppers into the experimental solution, not from the substrate (Figure S3).

To gain further insight into the mechanism, we fitted the kinetics to obtain initial substrate degradation rates \( p_{\text{parent}}^\text{in} \) in μM h⁻¹ and initial CO production rates \( R_{\text{CO}}^\text{in} \) in μM h⁻¹; Figures S6 and S7, Table S2). We found a strong positive correlation (R² = 0.97, N = S) between \( R_{\text{parent}}^\text{in} \) and \( R_{\text{CO}}^\text{in} \) for...
models with at least one ArOCH₃ group, regardless of their α-carbon functionality (Figure 3). In this analysis, we also included vanillic acid, a guaiacyl monomer with an absorption onset intermediate between G1 and G2 (Figure 2B). From the linear regression line, we obtained a slope of (5.7 ± 0.5)%, which represents the initial, mean YCO of the process. The fact that 6 h conversion efficiencies (Table 1) are higher than this value indicates that CO is not a first-generation product (Text S8, Figure S8).

The three guaiacyl α-alcohols had comparable R₀parent (10.5–19.0 μM h⁻¹) and R₀ values (1.65–2.00 μM h⁻¹; Table S2), which mirrors similarities in YCO values (Table 1) and absorption spectra (Figure 2B). These compounds were irradiated with 12 (instead of 6) UV lamps to speed up their photodegradation; as we expect blank CO production (i.e., the intercept of the regression line) to vary with light intensity, these data were not included in the regression analysis. In p-hydroxyphenyl models, the increase in Rparent did not lead to an enhanced ability to produce CO (Figure 3, black circles). Control measurements indicated that R₁CO for H1 and the blank were within their experimental error (0.218 (±0.009) vs 0.197 (±0.011) μM h⁻¹), while the value for H2 was slightly higher than the blank (0.41 (±0.02) μM h⁻¹), in agreement with 6 h YCO data.

Detection of Methanol Via ¹H NMR. Motivated by the correlation between the presence of ArOCH₃ functionalities and CO photoproduction, we collected evidence supporting the occurrence of formal hydrolytic demethylation, the substitution of a methoxy by a hydroxy group (Figure 1). We posited that the direct photolysis of guaiacyl and syringyl models releases methanol, while photodegradation of H1 and H2, which lack ArOCH₃ groups, do not. To evaluate this hypothesis, we irradiated a solution of each model compound in D₂O, and we followed the reaction via ¹H NMR as in Dallin et al.38

A qualitative analysis of ¹H NMR spectra during UV irradiation confirmed our hypothesis. Irradiated solutions of G and S models showed a singlet at 3.36 ppm, corresponding to CH₃OH (further confirmed with a methanol standard spike), with increasing intensity as a function of irradiation time (Figures 4A, S9B–F). This peak was not detected during irradiation of H2 and H1 (Figures 4B, S9A). In addition, all α-ketones produced acetate, while GD1 generated 1,2-propanediol (Table 1, Figure S9C). In almost all experiments, we detected acetone, but controls indicated its production to be an experimental artifact—as acetone was used to clean NMR tubes and caps prior to irradiation. In agreement with previous literature,38 the presence of acetone during irradiation had negligible influence on the results (Text S6.2).

Using the data at the end of irradiation, we calculated the CH₃OH conversion efficiency (YCH₃OH), defined as moles of methanol produced per moles of substrate degraded (eq 6). This calculation assumes that CH₃OH degradation is minimal during the experimental time span, which we confirmed experimentally (Text S6.2). This fact is not in contrast with the proposed mechanism, as we observed no OH* production at the high substrate concentrations used in these experiments (∼1 mM), likely due to light screening limitations (Text S6.2). We obtained YCH₃OH values of 19–36% and 73–74% for G and S models, respectively (Table 1), indicating that the number of ArOCH₃ groups defines the conversion efficiency. Like CO photoproduction, α-carbon functionality and presence of ancillary groups have a small influence on YCH₃OH. Further analyses revealed that concentrations of methanol and methoxy aromatic protons are always linearly correlated with the blank-corrected CO concentration after 6 h of UV irradiation (no mark, 6 lamps; 3, 12 lamps; n.s., not significant). CH₃OH conversion efficiencies (YCH₃OH) were obtained via eq 6 using the methanol concentration at the end of the experiment (no mark, 6 h irradiation; 3, 4 h irradiation; ††, 2 h irradiation; n.d., not detected). [OH]*₃HO were obtained from BA degradation via eq 7 (no mark) or were estimated from the p-hydroxybenzoate production rate of GD1 (*). All errors are obtained from error propagation.

| Table 1. Overview of the Main Photodegradation Products for the Lignin Model Compounds of Figure 2A* |
|-----------------------------------|-------------|-------------|-------------|-------------|-------------|
| compound | α-carbon | # -OCH₃ | GC analyses | ¹H NMR analyses | Rs analyses |
|---------|--------|--------|------------|----------------|-------------|
|         |        |        | YCO (%)    | YCH₃OH (%) | other products | [OH]*₃HO (10⁻¹⁰ M) |
| H1      | alcohol | 0      | n.s.       | n.d.         | ≈1.5*       | 4.5 ± 0.3 |
| G1      | alcohol | 1      | 11.5 ± 1.4 | 28.8 ± 3.2  | 3.7 ± 0.5   | 6.6 ± 0.3 |
| GD1     | alcohol | 1      | 11.7 ± 0.5 | 36.3 ± 1.1  | 1,2-propanediol | 5.4 ± 0.3 |
| GD2     | alcohol | 1      | 14.4 ± 0.2 | 18.7 ± 1.3  | ≈1.8*       | 7.0 ± 0.3 |
| S1      | alcohol | 2      | 10.2 ± 1.4 | 73.7 ± 2.3  | 4.7 ± 0.3   | 14.3 ± 1.0 |
| H2      | ketone  | 0      | 2.2 ± 0.7  | n.d.        | acetate     | 23.4 ± 1.5 |
| G2      | ketone  | 1      | 17.6 ± 2.1 | 23.1 ± 1.5  | acetate     | 31.0 ± 2.5 |
| S2      | ketone  | 2      | 11.2 ± 0.2 | 73.4 ± 1.4  | acetate     | 31.0 ± 2.5 |

*CO conversion efficiencies (YCO) were calculated via eq 4 with the blank-corrected CO concentration after 6 h of UV irradiation (no mark, 6 lamps; 3, 12 lamps; n.s., not significant). CH₃OH conversion efficiencies (YCH₃OH) were obtained via eq 6 using the methanol concentration at the end of the experiment (no mark, 6 h irradiation; 3, 4 h irradiation; ††, 2 h irradiation; n.d., not detected). [OH]*₃HO were obtained from BA degradation via eq 7 (no mark) or were estimated from the p-hydroxybenzoate production rate of GD1 (*). All errors are obtained from error propagation.
correlated ($R^2 \geq 0.94$; Figure S10), supporting the idea that 
CH$_3$OH is a first-generation product (Text S9, Figure S11).

Furthermore, the fact that $Y_{CH3OH > CH3CO} (19-74\% > 10.2-17.6\%)$ agrees with methanol being a precursor of CO and 
suggests that this gas is not its only oxidation product, in 
agreement with previous findings.

**Detection of Hydroxylated Photoproducts Via LC-HRMS Measurements.** Based on our proposed mechanism, 
formal hydrolytic demethylation leads to production of an 
aromatic hydroxy group (Figure 1). To confirm the occurrence 
of this process, we screened for 3-hydroxylated TPs via LC-HRMS 
(analysis performed only for G and S models). To 
increase the confidence of our results, we also collected MS$^2$ 
data and compared it to in silico predictions obtained with 
MetFrag.$^{57,59}$

MS signals corresponding to the expected TPs were detected 
for all tested compounds (Table S3, Figures S12–S17). Upon 
irradiation of G2, we observed a signal at m/z = 153.0550 
corresponding to the [M + H]$^+$ adduct of G2 TP1, the TP of 
formal hydrolytic demethylation (Figure 5). Its signal was 
detected at the same retention time (r.t.) of a commercial 
standard analyzed under the same conditions, and its MS$^2$ spectrum was in good agreement with the standard and in silico 
predictions (Figure S12F). We also detected 3-hydroxylated TPs during irradiation of G1 (m/z = 137.0601, detected as [M - H$_2$O + H]$^+$; Figure S13) and GD2 (m/z = 257.0828, detected as [M - H]$^+$; Figure S14). For the two syringyl 
compounds, we observed both the mono- and bis-demethyl-
ated species (Figures S15 and S16), which mirrors their higher 
$Y_{CH3OH}$ values as compared to G models (Table 1). For GD1, 
the only compound without a free phenol, we observed loss of 
both alkoxy substituents (Figure S17), in agreement with 
detection of both methanol and 1,2-propanediol via $^1$H NMR 
(Table 1). For monomeric compounds, the formation of 3-
hydroxylated TPs was assessed with relatively high confidence 
(level 1−2 according to Schymanski et al.$^{59}$), while for GD1 
and GD2, the confidence was lower (level 3−4; Table S3).

During irradiation of some G models, we also observed hydroxylated TPs that retained the ArOCH$_3$ group. When 
irradiating G2, we also detected m/z = 183.0656 at two 
different retention times. We assigned the signal at 11.5 min to 
the 5-hydroxylated species (G2 TP2a; Figure 5B) based on 
similarities in r.t. and MS$^2$ spectrum with the mono-

demethylated product of S2, while the second can be the 2-
or 6-hydroxylated species (G2 TP2b/c; Figure 5B). For 
G1, we only observed the 2- and 6-hydroxylated products (G1 
TD2a/b; Figure S13), while for GD2, we observed mono-
g (GD2 TP2a/b) and bis-hydroxylation (GD2 TP3; Table S3). 
These additional products were not detected during irradiation 
of GD1 nor for syringyl models.

**Figure 4.** $^1$H NMR spectra of G2 (A) and H2 (B) in D$_2$O during 4 h 
of UV irradiation (dark gray traces). At the end of the experiment, we 
added methanol (+0.18 mM) to confirm its occurrence as a reaction 
product (orange traces). Gray areas represent CH$_3$OH (3.36 ppm), 
blue areas denote the internal standard (CH$_3$SO$_3^-$, 2.81 ppm), and 
orange areas represent the resonance range of ArOCH$_3$ protons. 
Additional relevant signals are indicated with a filled circle (acetate, 
2.03−2.08 ppm) or an empty circle (acetone, 2.23 ppm). Note that 
acetone is not a reaction product. $^1$H NMR spectra of other substrates 
are in Figure S9.

**Figure 5.** (A) Kinetic traces of G2 and relevant degradation products detected via LC-HRMS as [M + H]$^+$ adducts (12 UV lamps). All traces are 
reported in normalized areas to aid comparison; absolute areas and MS$^2$ data are in Figure S12. (B) Schematic of the photodegradation process of 
G2 based on the data in panel (A). Note that three different isomers can have m/z = 183.0656; when possible, structures are assigned based on 
differences in retention time. Data for other substrates are given in Figures S13–S17.
A qualitative analysis of the signals’ kinetics indicates that all detected TPs are photolabile; thus, they are transient intermediates. All species showed growth-and-decay kinetics, and their signal intensity was typically 2–3 orders of magnitude smaller than the corresponding substrate (Figures S12–S17). For G2 TP1, the only compound for which a commercial standard was available, we calculated a maximum concentration of 0.36 μM after 20 min of irradiation, corresponding to \([G2 \text{ TP1}]_{\text{max}}/[G2]_0 = 7 \times 10^{-3}\). The photochemical instability of G2 TP1 was further confirmed experimentally by irradiating a solution of this compound in deionized water, obtaining direct photolysis rate constants of \((10.7 \pm 0.1) \times 10^{-3} \text{ min}^{-1}\) and \((12.1 \pm 0.3) \times 10^{-3} \text{ min}^{-1}\) for G2 TP1 and G2, respectively.

**Detection of Hydroxyl Radicals.** The second step of the proposed mechanism involves methanol oxidation to CO (Figure 1). As methanol does not absorb UV light, we hypothesized that reactive intermediates formed during photodegradation of lignin models trigger this reaction. We focused on the hydroxyl radical (OH\(^*\)) due to its well-acknowledged reactivity with methanol, both in laboratory and environmental settings. Literature precedents also indicate that OH\(^*\) can be produced during irradiation of hydroxybenzoic acids.\(^{53,64,65}\) To investigate whether the substrates of this study can be sources of OH\(^*\), we used BA as a hydroxyl radical probe.\(^{65,66}\)

Our measurements confirmed that UV irradiation of lignin model compounds produces OH\(^*\). Most substrates induced a measurable BA depletion, which could be fitted to a monoeponential decay function \((R^2 = 0.90–0.98; \text{Figure S18})\) to yield \([\text{OH}^*]_{\text{eq}} = 2.6–31.0 \times 10^{-16} \text{ M (eq 7; Table 1)}\). H1 and GD2 did not induce significant BA loss but produced \(p\), \(m\), and \(o\)-hydroxybenzoic acids, the expected photodegradation products,\(^{63}\) in experiments employing higher BA concentration (Figure S19). Compared to the other substrates, hydroxylated products were generated in lower concentrations, indicating that lack of BA decay was caused by OH\(^*\) production below the method’s detection limit. For H1 and GD2, we used the \(p\)-hydroxybenzoic acid production kinetics to estimate \([\text{OH}^*]_{\text{eq}} = 1.5–1.8 \times 10^{-16} \text{ M (Table 1)}\).

Control experiments further corroborated the formation of OH\(^*\). We first confirmed the photochemical stability of BA under UV light (Figure S18) and that hydroxylated products cannot be produced when the probe is irradiated in the absence of lignin models (Figure S19). We also irradiated each substrate in the presence of BA and isopropanol (1% \(v/\) \(v\)), a common OH\(^*\) quencher, observing suppression of the probe’s decay (Figure S18). The latter further hints that BA is degraded by free OH\(^*\), not by other hydroxylating species or reactive intermediates,\(^{3,67,68}\) similar to what was reported for other hydroxybenzoic acids.\(^{64}\)

**DISCUSSION**

**Step 1: Formal Hydrolytic Demethylation of Lignin Model Compounds Via Direct Photolysis.** \(^{1}\)H NMR and LC-HRMS measurements provided unequivocal evidence for the occurrence of formal hydrolytic demethylation via direct photolysis. All G and S models produced CH\(_3\)OH (Figures 4, S9) and the corresponding 3-hydroxylated TP (Figures S12–S17) regardless of their \(\alpha\)-carbon oxidation state or presence of ancillary substituents, while CH\(_3\)OH was not detected during irradiation of compounds lacking the ArOCH\(_3\) group. In addition, \(Y_{\text{CH3OH}}\) values of S compounds (73–74%) were considerably higher than G models (19–36%; Table 1); correspondingly, MS data revealed that both mono- and bis-demethoxylated products formed during irradiation of S1 and S2 (Figure S15 and S16). Thus, all available information is consistent with CH\(_3\)OH originating from cleavage of ArOCH\(_3\) groups. Notably, CH\(_3\)OH is also a major microbial degradation product of lignin,\(^{69}\) which is in agreement with the recent work by Nalven et al.\(^{70}\) showing that sunlight and microbial enzymes induce similar chemical changes in DOM.

Based on the available data, we speculate that CH\(_3\)OH is released via the same pathway proposed by Dallin et al.\(^{38}\) for syringic acid: excited state protonation of the aromatic ring followed by nucleophilic attack by water and subsequent loss of CH\(_3\)OH via Ar-OCH\(_3\) cleavage (eq 1). While confirmation of this hypothesis requires a dedicated study, our observations favor alternative options, namely, ArO-CH\(_3\) cleavage followed by CH\(_4\) release (reported in vacuum in the solid state)\(^{40}\) and OH\(^*\)-induced cleavage (reported during fungal demethylation\(^{69}\) and chemical oxidation\(^{83}\)). Specifically, \(^{1}\)H NMR measurements showed that CH\(_3\)OH is a major product \((Y_{\text{CH3OH}} = 19–73%)\) and that it is produced via an apparent one-step reaction (Figures S10 and S11) under conditions that would favor CH\(_4\) accumulation, that is, when OH\(^*\) is not formed (Figure S4B). Furthermore, the occurrence of hydroxylation at multiple ring sites (e.g., G2 TP2a/b/c; Figure 5) and the detection of products originating from cleavage of other aromatic functionalities (i.e., 1,2-propanediol and acetic acid; Table 1) hint that all sterically accessible ring locations, and not only the ones adjacent to the ArOCH\(_3\) group, may undergo this process. Finally, control experiments showed minimal changes in substrates’ photodegradation kinetics in the presence and absence of isopropanol (Figure S20), ruling out OH\(^*\) as a major trigger of hydrolytic demethylation. Note that formation of hydroxylated products without the intermediacy of OH\(^*\) is not uncommon during direct photolysis of aromatic compounds.

**Step 2: Methanol Oxidation to CO Via Indirect Photolysis.** Even though CO and OH\(^*\) production data support the occurrence of the second step (i.e., CH\(_3\)OH + OH\(^*\) → CO), more work is needed for its confirmation and for uncovering its mechanistic details. Literature precedents show that methanol oxidation in water is a complex process, as its kinetics and product yields depend on CH\(_3\)OH concentration, pH, \([\text{OH}^*]_{\text{eq}}\) and presence of other radicals.\(^{44,74}\) Furthermore, gas-phase studies suggest that CO is generated via oxidation of formaldehyde,\(^{27,46}\) a methanol oxidation product in both aqueous and gas phase,\(^{44,46,74}\) not directly from CH\(_3\)OH. Thus, detection of OH\(^*\) radicals during UV irradiation of lignin model compounds only indicates that this reaction is plausible but falls short of definitive proof. In addition to OH\(^*\), other reactive intermediates formed during photodegradation of lignin model compounds may trigger the conversion of CH\(_3\)OH to CO. While we discarded singlet oxygen and triplet excited states due to their low reactivity toward methanol,\(^{57,76}\) peroxo radicals may play a more important role.\(^{77–79}\) Peroxy radicals form when a carbon-centered radical reacts with oxygen\(^{80}\) and have been detected during photooxidation of lignin and its model compounds (reviewed by Heitner\(^{81}\)). OH\(^*\) oxidation of methanol,\(^{44,74}\) and DOM photolysis.\(^{82}\) Ongoing work in our lab is elucidating identity and yields of CH\(_3\)OH photooxidation products under conditions relevant to sunlit surface waters.
Limitations of this Work. The use of simple substrates is an intrinsic limitation of all model compound studies. In this work, we mitigated this drawback by mimicking as accurately as possible the key structural elements of natural lignin (Figures 1 and 2A). Furthermore, our results strongly suggested that the proposed mechanism is controlled by the chemical structure of the aromatic core unit, which is the same in our models and in the natural polymer. As a matter of fact, the three guaiacyl α-alcohols (G1, GD1, and GD2) always showed the same reactivity pattern. Lignin is also known to depolymerize during photodegradation, thereby releasing monomers with the same aromatic core units of our models. Indeed, irradiation of GD1 released 1,2-propanediol (Table 1) and formed GD1 TP2 (Figure S17), the same TP detected during irradiation of G1 (i.e., G1 TP1; Figure S13). Gao and Zepp also showed that that low-molecular-weight fractions (<1 kDa) have 2.5–3 times higher apparent CO quantum yields than unsubfractionated DOM, which fits with the yet untested hypothesis that the proposed mechanism is mostly effective after (partial or total) depolymerization. Thus, despite the promising results, follow-up investigations need to confirm our findings using natural lignin.

Additional limitations include substrates’ concentrations and the use of deionized water as solvent. The choice of 50 μM (i.e., 6.9–14.5 mg L\(^{-1}\) or 4.8–9.6 mgC L\(^{-1}\)) as our initial concentration was dictated by the constraints of the CO measurement setup, that is, the \(\approx 1 \mu\text{M} \text{CO background and } Y_{\text{CO}} \text{ values of } 2–18\%\). Depending on the selected lignin proxy, these concentrations are either comparable or at least one order of magnitude higher than natural lignin (Section S10). Whereas we expect variations in concentration to have minimal impact on the direct photolysis step, rates and yields of methanol oxidation to CO may change. This step is also susceptible to matrix variations, including nature and concentrations of salts, metals, and additional DOM components (see the previous section). Solution temperature is an additional variable that can influence methanol oxidation to CO, as we propose this to be a bimolecular reaction. Apparent CO quantum yields of DOM have a temperature dependence; confirming this dependence in our model system can help to establish its environmental relevance.

Environmental Significance. This work presents data supporting the role of ArOCH\(_3\) groups as the precursors of CO via a two-step mechanism involving a combination of direct and indirect photolysis. This result builds on previous work by Stubbins et al. and, to the authors’ knowledge, is the first explicit mechanism justifying CO production from DOM photodegradation. Albeit further investigations need to confirm its natural occurrence and elucidate specific mechanistic details, this work sets the basis for the development of predictive models directly applicable to DOM. A key finding is that initial CO photoproduction rates can be predicted from the initial substrate photodegradation rate and the substitution pattern of the aromatic core unit (Figure 3). If this correlation proves valid also for natural lignin and DOM, it will allow estimating CO photoproduction rates from the number of G + S core units and the direct photolysis degradation rate, two parameters that can realistically be obtained using established techniques (e.g., Yan and Kaiser). This information will allow one to predict variations in apparent CO production quantum yields as a function of DOM type and thus improve current estimates of photochemical CO production in coastal regions and freshwaters. These environments are potential production hotspots not accurately described in global CO production models, which rely on apparent CO quantum yield parametrizations based on marine data.

An unanticipated finding of our work is the potential of lignin to act as the precursor of CH\(_3\)OH and other C\(_1\)-containing compounds, and as a source of OH\(^*\). So far, CH\(_3\)OH has not been reported as a DOM photodegradation product, even though its formation was hypothesized. The few studies investigating this process focused on the ocean, where DOM and lignin concentrations are low and thus where their contribution is easy to overlook. To the authors’ knowledge, photoproduction of CH\(_3\)OH from terrestrial DOM has never been reported nor investigated, perhaps due to analytical difficulties in detecting this alcohol and/or the presence of removal mechanisms (e.g., OH\(^*\) oxidation) that rapidly consume it. Given lignin’s abundance in terrestrial DOM and the high methanol yields that we measured, a reassessment of photochemical CH\(_3\)OH sources is warranted.

The proposed mechanism may also represent a possible production pathway of formaldehyde, formic acid, and CO\(_2\), abundant and ubiquitous DOM photoproducts. Previous authors showed that irradiation of quinones, mono- and diphenols, hydroxybenzoic acids, and hydroxybenzoic aldehydes can produce OH\(^*\) and/or other hydroxylating species. For quinones, a mechanism involving an exciplex between triplet excited states and water has been proposed. An alternative hypothesis that has not yet been thoroughly considered (albeit once proposed) is that hydroxyl radicals are generated during photolysis of hydroxylated aromatics. This hypothesis fits with the general understanding that (at least part of) OH\(^*\) in sunlit surface waters form during the photodegradation of aromatic components of DOM and that model compounds that generate OH\(^*\) are typically degraded during irradiation. Dallin et al. also proposed that, in addition to releasing methanol, the intermediate formed after excited state protonation of syringic acid releases OH\(^*\) and forms another of their observed products. Furthermore, C-centered radicals formed during lignin photodegradation (e.g., upon H-abstraction from α-alcohols) can react with O\(_2\) yielding a peroxo radicals, which further fragment to form α-carbonyls and superoxide radicals. The latter can dismutate to yield H\(_2\)O\(_2\), a precursor of OH\(^*\), and H\(_2\)O. These unforeseen insights on long-standing questions related to DOM photochemistry call for a thorough reassessment of the light-triggered reactivity of lignin and its degradation products in aquatic systems.

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Sources and synthetic procedures of used chemicals; compound speciation at the experimental pH; supplementary details; graphs, and tables on experiments detecting CO, methanol, hydroxylated transformation products, and OH*; description of control experiments; details of UPLC methods; supplementary calculations on kinetic parameters; and estimation of lignin concentrations in natural waters. (PDF)

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