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Letter

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Insights into the photoproduction sites of hydroxyl radicals by dissolved organic matter in natural waters

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ABSTRACT

The hydroxyl radical (•OH) is the most reactive oxidant produced in natural waters. Photoproduction by chromophoric dissolved organic matter (CDOM) is one of its main sources, but the structures responsible for this production remain unknown. Here, a series of substituted phenol model compounds are examined to test whether these structures could act as a source of •OH. We find that many of these compounds do produce •OH with quantum yields (Φ) ranging from ~10^{-4} to ~10^{-2}. In particular, two compounds that have hydroxy groups and carboxyl groups in a para relationship (4-hydroxybenzoic acid and 2,4-dihydroxybenzoic acid) exhibit relatively high Φ, ~10^{-2}. For 2,4-dihydroxybenzoic acid, the formation of •OH was confirmed through use of competition kinetics and reaction with methane. We conclude that these types of structures, which may derive from polyphenolic source materials such as lignins, tannins and humic substances, could be an important source of •OH in natural waters.

TEXT

INTRODUCTION

The highly reactive hydroxyl radical (•OH) acts to degrade both natural and anthropogenic compounds in the environment, and also impacts the health of aquatic microorganisms. Known sources of •OH in natural waters include nitrate and nitrite photolysis, Fenton and Fenton-like reactions, and photoreactions of chromophoric dissolved organic matter (CDOM).[1-3] Although it has been known for some time that CDOM produces •OH by a direct photochemical pathway,[4] the organic moieties within the CDOM that produce •OH are still unknown. Earlier work indicated that quinone moieties within humic substances (HS) might be involved[4,5] based on the observation that irradiation of quinone model compounds in the presence of chemical probes for •OH produced products characteristic of •OH reaction.[6-9] However, a series of later studies provided strong evidence that •OH is not produced by most quinones,[9-13] but instead that another oxidative intermediate is responsible for the observed •OH probe reactions.[9,13] This oxidative intermediate could result in an overestimation of the observed •OH production rates measured by some probes in natural waters.[1,2,4] Available evidence, however, also indicates that photoproduction of •OH production from CDOM is restricted to the UV-B and far UV-A wavelengths,[5,14] whereas many quinones have their lowest-lying absorption band in the near UV-A or visible wavelengths[15] where the observed •OH photoproduction is not detected. Finally, it was also noted that quinone concentrations as determined electrochemically within HS[16,17] appear to be too low to support this production.[14] Thus, quinone moieties within HS cannot be the main •OH source, and the types of structural moieties responsible for •OH production by CDOM remain unknown.[14]

To examine this question, the quantum yields for •OH production (Φ) were acquired for a series of mono- and di-substituted phenols as model constituents of HS and CDOM, as well as possible constituents produced by oxidative modification of polyphenolic source materials such as the lignins and tannins. Experiments employing competition kinetics and reaction with methane were conducted to test whether •OH was indeed formed.

EXPERIMENTAL

Chemicals

Chemical specifications are detailed in the supporting information.

Methods

Irradiation. We examined eleven model compounds (20 μM), including five dihydroxybenzoic acids (DHBA), three hydroxybenzoic acids (HBA), two resorcinols (RS and 4-ethyl-RS), and one dihydroxybenzaldehyde (Fig. 1). The quantum yields (Φ) were measured using a 3 cm cuvette and an Oriel tunable light source composed of a 1000 W xenon lamp and grating monochromator (Model 77200; 10 nm bandwidth). The competition and methane trapping experiments as well as the 2,4-DHBA photodegradation experiment were conducted employing a solar simulator with a spectral output nearly identical to natural sunlight from ~295 to ~360 nm.[18,19] The buffer solution was 5 mM phosphate (pH 7).

•OH formation rate (R_{OH}). Initial rates of phenol formation R_{ph} (μM/h) were determined by HPLC[18] using benzene as the probe at a concentration sufficiently high (1 mM) to ensure complete reaction with •OH. Initial rates of •OH formation, R_{OH} were then obtained as follows:

$$R_{OH} = \frac{R_{ph}}{Y_{ph}} \qquad (1)$$

where Y_{ph} is the yield of photoproduct formed from benzene by reaction with •OH; the value of Y_{ph} for benzene is 0.69.[18]

•OH quantum yields (Φ). Φ were measured at wavelengths extending across the lowest-lying absorption band of the model compounds, but within the range of the solar spectrum, 290~340 nm; most compounds studied have negligible absorption above 350 nm (Fig. S1). Φ were determined from the relation:

$$\Phi = \frac{R_{\mathrm{OH}}}{P_{\lambda}(1-10^{-A})} \qquad (2)$$

where A is the absorbance of the model compounds in a 3 cm cuvette. P_{λ} (einstein $L^{-1}h^{-1}$) is the volume irradiance, which was calculated as followed:

$$P_{\lambda} = \frac{\Delta n}{\Phi_{\lambda} t(1-10^{-A})} \qquad (3)$$

where Δn is ferrous iron photo-generated (moles L^{-1}) as measured from the concentration of the Fe(II) trisphenanthroline complex, t is the irradiation time (h), and Φ_{λ} is potassium ferrioxalate quantum yield, which was obtained from the *Murov's Handbook of Photochemistry*.[20] The value of 1.24 was used for Φ_{λ} in the wavelength rage 280~310 nm.

Methane trapping reaction. 3-amino-2,2,5,5,-tetramethyl-1-pyrrolidinyloxy free radical (3-ap) was added to the samples (model compounds or sodium nitrite in 20 mM borate buffer at pH 8) in a 4 mL septum vial to a final concentration of 100 µM. The mixture was flushed with nitrogen for 5 min to remove dioxygen, and then with methane for 10 min. The vial was then irradiated in the solar simulator. After 2 h irradiation, 1 mL of the solution was mixed with 200 µL 2.5 mM fluorescamine and analyzed by HPLC.[5] As a control, the photolysis of nitrite was employed as a known •OH source.[5]

Competition experiments. A series of concentrations (0.5 mM to 3 mM) of the competitors, formate or DMSO, were added to solutions of the •OH probes, either 1 mM benzene or 1 mM benzoate. Because benzoate is not be completely selective for OH,[4,21] this probe was employed in the competitions experiments as an additional test for the sole presence of OH; i.e., if both OH and another oxidative intermediate were present, the competitive kinetics (and rate constant ratios) would not be consistent with those of OH alone. [4,21] Formate, benzene, DMSO, and benzoate react with •OH at reaction rates of k_f (3.2×10^9), k_{be} (7.8×10^9), k_{DMSO} (7.0×10^9) and k_{ba} (4.3×10^9), respectively.[22] The decrease in the initial rate of product formation in the presence of increasing concentrations of the •OH competitor can be obtain from the following equation:[23]

$$R_n = R_0 \times \frac{k_p[\text{Probe}]}{k_c[\text{Competitor}] + k_p[\text{Probe}]} \qquad (4)$$

where [Probe] and [Competitor] are the concentrations of probe and competitor, respectively, R_n is the initial rate of product formation from the probe at different competitor concentrations (either formate or DMSO), and R_0 is the initial rate of product formation from the probe in the absence of the competitor. The ratios of the •OH rate constants can then be obtained from the following expression:

$$\frac{R_0}{R_n} = 1 + (k_c/k_p)([\text{Competitor}]/[\text{Probe}]) \qquad (5)$$

Plotting R_0/R_n against [Competitor]/[Probe], a straight line was obtained (Fig. S2-S4, right panels). The rate constant ratios (k_f/k_{be}, k_f/k_{ba}, and k_{DMSO}/k_{ba}) were calculated from the slopes. The experimental rate constant ratios were compared for irradiated solutions of 20 µM 2,4-DHBA and 100 µM H_2O_2 under solar simulator at the same condition, the latter being a known •OH source.

RESULTS AND DISCUSSION

Two of the model compounds, 2,6-DHBA and 3-HBA, showed no evidence of •OH production (Table 1; Fig. S5). Of the nine remaining compounds, the highest Φ were observed for 2,4-DHBA and 4-HBA (both ~10^{-2} at 310 nm), followed by 2,5-DHBA, 3,4-DHBA, RS and

4-ethyl-RS (~10^{-3}), and 2,3-DHBA, 2-HBA and 2,4-DHA (all ~10^{-4}). The Φ showed no obvious pattern with structure. For example, although 2,4-DHBA and 4-HBA exhibited the highest Φ and have hydroxy groups and carboxyl groups in a para relationship, 3,4-DHBA, which also contains this substitution pattern, exhibited a value of Φ over an order of magnitude lower. Although the structural basis of this •OH generation is not yet clear, these results clearly show that many mono- and di-substituted phenols are capable of producing •OH at levels consistent with environmental samples.

To ensure that •OH was indeed the intermediate being detected, methane was employed in place of benzene as a more selective probe.[13,24] Methane reacts with •OH to form the methyl radical (k=1.2×10^8M-^{1}s^{-1}), which can then be selectively trapped by a stable nitroxide radical, converted to a fluorescent derivative and measured by HPLC.[13,24] Irradiation of 2,4-DHBA in the presence of methane produces this fluorescent derivative, providing very strong evidence that •OH is the reactive species being generated (Fig. S6).

In addition, to confirm further that this species was •OH, the effect of added competitors, formate and dimethylsulfoxide (DMSO), on the rates of product formation from the probes, benzene and benzoate, were examined for 2,4-DHBA. The results (Table 2) show that the rate constant ratios acquired from these competition experiments are consistent not only with the published ratios for •OH but also with those obtained using the photolysis of H_2O_2 as a known •OH source. These rate constant ratios differ markedly from those observed for quinone model compounds, providing further evidence that these compounds do not produce •OH.[9,13]

The mechanism(s) by which •OH is produced photochemically from these DOM model compounds is currently unclear. The presence of a carboxyl group appears to be important in a few cases, because substituting either a proton, aldehyde or ethyl group for the carboxyl greatly decreased the Φ relative to 2,4-DHBA and 4-HBA (see RS, 4-ethyl-RS, and 2,4-DHA in Table 1). Under conditions of low 2,4-DHBA loss (≤20%), the stoichiometry of •OH formation to 2,4-DHBA loss (in the absence of probes) was found to be approximately constant, having a value of ~0.25 (Fig. S7). This relatively high stoichiometric value for OH formation under low reactant conversion suggests that •OH formation is not arising from secondary photochemical reaction(s) of a product, at least for this compound. Similarly, the almost constant values of Φ observed at wavelengths across the lowest-lying absorption bands of these compounds (Table 1) suggest that the photochemistry is arising from a single state. The reaction also appears to be water dependent because •OH was not produced from 2,4-DHBA in dry acetonitrile. Importantly, the detection of •OH from 2,4-DHBA under anoxic conditions (atmosphere of methane; Fig. S6) indicates that it is produced via a dioxygen-independent pathway similar to that observed previously for HS.[5]

As phenols are known to photoionize in water through both monophotonic and biphotonic processes,[25] one hypothetical mechanism consistent with these observations would involve an initial photoionization step to form the hydrated electron e^-_{aq} and the corresponding phenol cation radical or secondarily, the phenoxy radical following deprotonation,[26] followed by the elimination of •OH. Alternatively, rapid nucleophilic addition of H_2O to the cation radical could form a dihydroxycyclohexadienyl radical intermediate from which •OH then eliminates.[27-29] Interestingly, apparent Φ for hydrated electron[30] and •OH[5] formation from HS are not only similar in magnitude, but also occur over a similar spectral range in the UV-B and far UV-A, implying that their formation may be coupled.

Another hypothetical mechanism for compounds containing -OH and either a -COOH or -CO in the para position (e.g., 2,4-DHBA) may involve formation of a triplet state quinoid enol tautomer through excited state proton transfer,[31,32] which subsequently abstracts a H-atom from the hydrogen bonded water to form •OH in a manner similar to that proposed for quinones.[7,8] However, as with that mechanism, there is currently little evidence that •OH could be formed through this pathway. Elucidating the detailed mechanism(s) of •OH formation from these DOM model compounds remains an important area for future investigation.

In most cases, the *apparent* Φ measured for CDOM and HS $(3\sim8)\times10^{-5}$ [5,33] are significantly lower than the Φ acquired for the model compounds. However, *apparent* Φ are based on the total numbers of photons absorbed by the CDOM and not on the number of photons absorbed by the photoactive constituent. Because many of the structures producing •OH (Table 1) may well be minor contributors to the total CDOM absorption, the lower apparent CDOM yields are readily explainable. Importantly, the model compounds produce significant yields of •OH over the range of wavelengths in the UV-B and far UV-A where •OH is known to be produced by HS and CDOM.[5]

Our results suggest that substituted phenols, specifically certain carboxylate-substituted phenols, are important sources of photochemically produced •OH within CDOM. These structures are commonly present in HS.[34,35] For instance, fulvic and humic acids originating from soil contain a large proportion of benzenecarboxylic and phenolic compounds, which are primarily derived from lignin degradation and transformation.[35] Moreover, these structures can be formed via photochemical modification of polyphenolic precursors. For example, the acid–to-aldehyde ratio of lignin phenols increases during irradiation of isolated from both natural waters and HS (isolated from the Congo River) indicating oxidative conversion to phenolic acids.[36] In addition, ring hydroxylation by •OH is well documented (e.g., benzoic acid hydroxylation[23]) and undoubtedly occurs to DOM phenolic moieties during solar irradiation. We conclude that these types of structures are likely important sources of •OH in many natural waters, particularly those with low concentrations of other •OH sources, such as nitrate, nitrite and Fenton reactants.

ASSOCIATED INFORMATION

Supporting Information

Additional figures, tables, and details of chemicals.

This material is available free of charge via the Internet athttp://pubs.acs.org.

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Notes.

The authors declare no competing financial interest.

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FIGURES

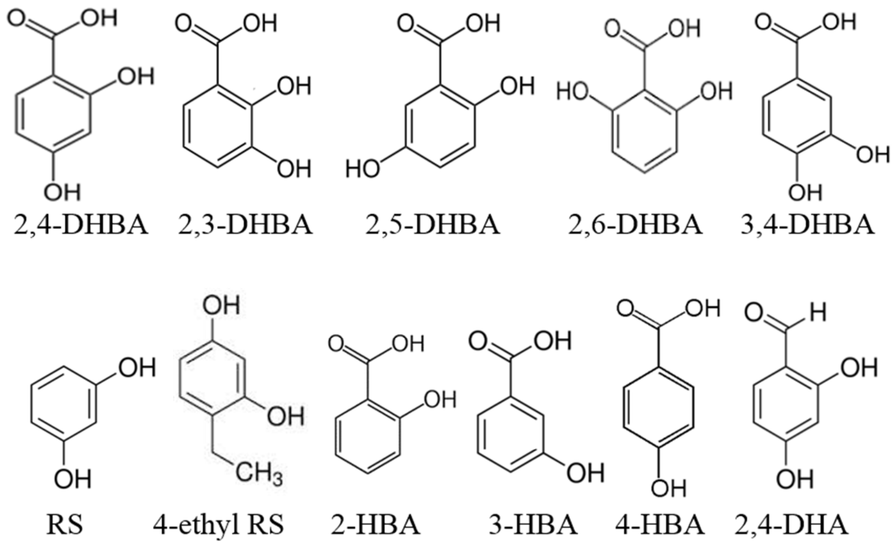

Fig. 1. Structures of the eleven model compounds examined. NOTATION: DHBA- dihydroxybenzoic acid, HBA - hydroxybenzoic acid, RS-resorcinol, DHA- dihydroxybenzaldehyde.

Table 1. Quantum yields (Φ) of 20 μM model compounds using benzene (1 mM) as the probe for wavelengths from 290 to 340 nm at pH 7.

	$\Phi\times10^3$ at each wavelength					
	290 nm	300 nm	310 nm	320 nm	330 nm	340 nm
2,4-DHBA∗	9.8±0.1[a]	8.0±0.1	12.9±0.4	8.9±1.2	NM[b]	NM
3,4-DHBA	0.73±0.13	0.78±0.14	2.5±0.2	1.0±0.3	NM	NM
2,5-DHBA	1.4±0.1	1.1±0.1	0.47±0.09	0.20±0.03	0.08±0.02	N/A[b]
2,3-DHBA	0.86±0.23	0.40±0.04	0.26±0.06	0.15±0.01	ND	ND
2,6-DHBA	ND	ND	ND	ND	ND	ND
2,4-DHA	ND	0.13±0.02	0.15±0.02	0.10±0.01	ND	ND
	280 nm	285 nm	290 nm	300 nm	310 nm	
4-HBA	10.0±0.4	10.3±0.6	11.3±1.2	NM	NM	
2-HBA	0.62±0.09	0.41±0.16	0.54±0.12	0.17±0.09	NM	
3-HBA	ND	ND	ND	NM	NM	
RS	2.1±0.3	1.9±0.4	NM	NM	NM	
4-Ethyl-RS	2.1±0.3	1.5±0.2	2.2±0.4	NM	NM	

∗DHBA-dihydroxybenzoic acid, HBA-hydroxybenzoic acid,

DHA-dihydroxybenzaldehyde, RS-resorcinol

[a] Mean value from two measurements. The ± represents the range.

[b] The symbol NM means that Φ was not measured due to low absorbance($<5\times10^{-3}$) (Fig. S1).

[c] The symbol ND means •OH production was under the detection limit (1.2 nM).

Table 2. Rate constant ratios of formate to benzene (k_f/k_{be}), formate to benzoate (k_f/k_{ba}) and DMSO to benzoate (k_{DMSO}/k_{ba}).

	2,4 DHBA as source	H_2O_2 as source	Value calculated from the literature[21]
k_f/k_{be}	0.62±0.01*	0.64±0.04	0.41~0.56
k_f/k_{ba}	0.60±0.01	0.55±0.03	0.45~0.56
k_{DMSO}/k_{ba}	1.00±0.06	1.11±0.06	1.12~1.23

*: Mean value from two measurements. The ± represents the range.

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