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Selectivity in the photo-Fenton and photocatalytic hydroxylation of biphenyl-4-carboxylic acid and derivatives (viz. 4-phenylsalicylic acid and 5-phenylsalicylic acid)

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The selectivity of hydroxylation of the distal rings of 4-phenylbenzoic acid, 4-phenylsalicylic acid, and 5-phenylsalicylic acid were determined using partial TiO_2-mediated photocatalytic degradation and photo-Fenton conditions. This separation of the binding site from the phenyl group being hydroxylated allows a less-biased evaluation. The hydroxylation regiochemistry behaves as qualitatively expected for an electrophilic reaction, given the assumption that 4-carboxyphenyl is a slightly electron-withdrawing substituent. Selectivity for hydroxylation of the distal phenyl in 4- and 5-phenylsalicylic acid is reversed, due to the reversal of the electronic demand, while adsorption to the TiO_2 surface is assumed to be analogous for the two structures. Copyright © 2011 John Wiley & Sons, Ltd.

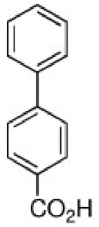
Supporting information may be found in the online version of this paper.

Keywords: hydroxylation; photocatalysis; photo-Fenton; selectivity; titanium dioxide

INTRODUCTION

The study of the early oxidation steps of organic molecules under conditions of TiO_2-mediated photocatalytic degradation has been fruitful, at first to understand the chemistry of the mineralization process, and more recently as a probe to explore differences among catalysts. Broadly, hydroxyl-like chemistry and chemistry driven by single electron transfer (SET) are the two commonly observed modes of reactivity, particularly for aromatic organics.[1–13] Compounds with multiple reactivity modes become useful interrogators of other catalysts; for example we and others have used 4-methoxyresorcinol, quinoline, and 1-anisylneopentanol (1-(4-methoxyphenyl)-2,2-dimethylpropan-1-ol)) as probe molecules[14–18] to evaluate several modified and doped TiO_2 photocatalysts.[19–23]

However, the balance of reactivity is determined not only by functionality, but also by the ability of the molecule to bind to the TiO_2 surface.[10,24–32] We wanted to add to our bank of test molecules, not least because we thought it important to have molecules with different binding modes. Thus the carboxylic acid functionality, common to organic water pollutants and their degradation intermediates was attractive. Here, we describe the partial degradations of biphenylcarboxylic acid derivatives **1**–**3** by TiO_2 and under photo-Fenton conditions used as a control for the hydroxyl-like chemistry.



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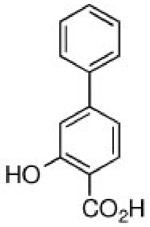

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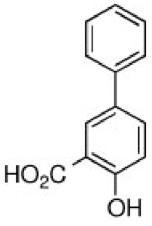

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4-Biphenylcarboxylic acid (**1**) was chosen as a starting point for a new probe molecule because it had both the desired functionality and some symmetry that would limit the number of products. We hypothesized that the geometry associated with adsorption through the carboxylate and the differing electron demands of the proximal (di-substituted) and distal

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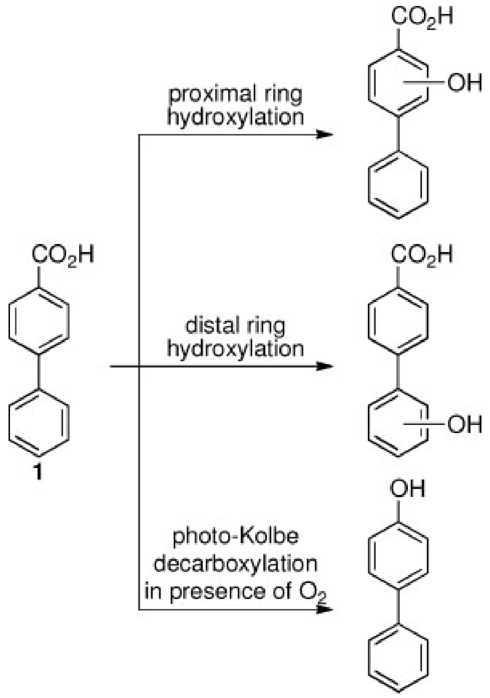
(mono-substituted) phenyl moieties might provide a basis for regiochemical selectivity for the SET and hydroxyl-like pathways. We posited that the comparison of **1** to 4-phenylsalicylic acid (**2**) and 5-phenylsalicylic acid (**3**) might prove useful, in that the additional electron richness of the proximal ring might further enhance SET chemistry. Moreover, to the extent that the relative arrangements of the substituents in **2** and **3** reverse – or at least modify – their electronic influence on the distal phenyl, it was possible that further differentiation might be observed.

A few publications address the regiochemistry of TiO_2-mediated and -related hydroxylations, and they broadly suggest that regiochemistry of TiO_2-mediated hydroxylation follows the qualitative rules familiar from standard electrophilic aromatic substitution.[33–39] However, the comparison of substituents necessarily combines the effects of adsorption ability and the electronic effect of the substituent. Compounds **2** and **3** are used to address this question without that ambiguity.

RESULTS AND DISCUSSION

Partial degradations of **1**–**3** were carried out using P25 TiO_2 at pH 8.5 and 12, and also using photo-Fenton conditions at pH 8.5. Solubility limited the ability to run the reactions at low pH, and previous experience had shown that 8.5 is a near-ideal pH for the observation of intermediates in degradations closely related to these.[28,29] At higher pH, the TiO_2 reactions could be done, but the photo-Fenton reactions could not be, due to precipitation of the iron. Three classes of initial reactions were expected under TiO_2 degradation conditions: (i) hydroxylation of the proximal ring, e.g., conversion of **1** to **2**; (ii) hydroxylation of the distal ring, e.g., conversion of **1** to **1c** (Chart 1); and (iii) reactions related to photo-Kolbe decarboxylation through SET at the carboxylate functionality. Previous studies on the degradation of benzoic acid all report formation of salicylic acid, with some reporting observation of other hydroxylated benzoic acids and small amounts of phenol.[39–44]



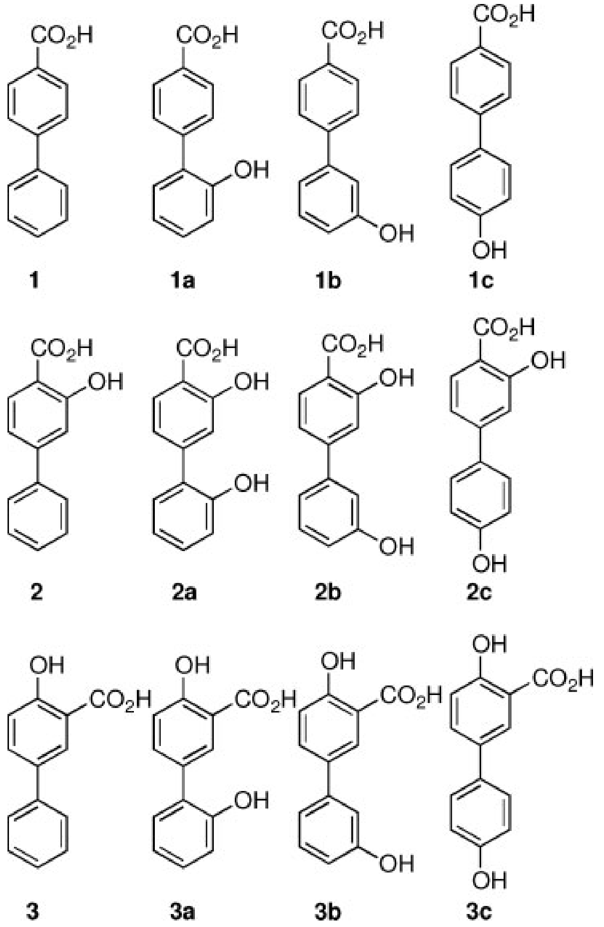


Chart 1. Starting biphenylcarboxylic acids and their hydroxylated derivatives.

Reasonable zero-order rates were obtained with conversions up to ~25% and are shown in Table 1. (Degradations to higher conversion began to resemble first order decays, as is common for photocatalytic degradations.) All runs were at least duplicated, and error limits in the table represent standard deviations from the average. Control experiments showed that no significant degradation occurred on the timescale of the experiments when the TiO_2 was omitted or if samples were not exposed to light.

The absolute rate constants, obtained with initial concentrations of 0.25 mM, depend on several experimental parameters, including lamp intensity, sample geometry, etc. However, all physical parameters were held constant for the TiO_2 reactions, so the relative rates are meaningful. Among them, the pH 12

Table 1. Initial rates of degradation of **1**–**3** using titanium dioxide at pH 12 and 8.5 and the photo-Fenton reaction at pH 8.5

	Rate of degradation (μM/min)		
Compounds	TiO_2 pH 12	TiO_2 pH 8.5	Photo-Fenton
1	15.1 ± 0.9	13.1 ± 0.7	1.4 ± 0.5
2	15.9 ± 1.0	10.7 ± 0.9	15.3 ± 1.0
3	17.2 ± 1.6	15.6 ± 0.6	14.2 ± 1.4

reactions showed no rate variations that could be firmly put outside experimental uncertainties, and the rates at pH 8.5 were all within a factor of about 1.5.

The rates obtained for the photo-Fenton reaction, used as a model for the hydroxyl-type reactivity in TiO_2 chemistry,[3,14,45,46] were coincidentally similar to those obtained for TiO_2-mediated degradations. However, they importantly showed a different internal rate profile, in that the rate obtained for degradation of **1** was an order of magnitude slower than that for the other two compounds. The simplest explanation for this is that the rates for the TiO_2-mediated reactions are limited by interactions with the TiO_2 surface, while the photo-Fenton reactions revealed rates that reflected more about the inherent reactivity of the compounds.

An alternate and perhaps more probable explanation for the slower removal of **1** under photo-Fenton conditions is based on the hypothesis that the *o*-hydroxycarboxylate functionality tends to chelate iron ions. Thus, compounds **2** and **3** are effectively better ligands for the iron ions than is **1**. As a result, **2** and **3** are degraded faster than **1** because the hydroxyl radicals are formed immediately in their vicinity. Whether truly free hydroxyl radicals are formed at all in Fenton chemistry is a matter of some controversy (e.g. Ref. [47]); however, the lack of a free hydroxyl radical would only reinforce this explanation. (The photochemical step of the photo-Fenton reaction is not presumed to be generation of hydroxyl, so the point remains.[48]) Indeed, **1c**, an isomer of **2** and **3** that does not have the *ortho* relationship between its hydroxy and carboxylate functionality, and it was shown (*vide infra*) to degrade at a rate quite similar to **1**, rather than comparable to **2** and **3**.

However, our primary interest was in the product distribution. Three monohydroxylated derivatives of each sharting material were prepared: the products of *ortho*, *meta*, and *para* hydroxylation of the distal phenyl group. They are illustrated in Chart 1 as the 'a', 'b', and 'c' derivatives of each compound, respectively. Compound **2** may be viewed as a hydroxylated derivative of **1**, but no other compounds with hydroxylation of **1**, **2**, or **3** on the ring proximal to the carboxylic acid were prepared. After degradation of 10–20%, samples were exhaustively silylated and examined by GC. Products were identified by their unique retention times (and by co-injection of the authentic samples) on GC and by GC-MS verification of the mass. No singly hydroxylated derivatives of **2** or **3** other than compounds **2a–c** and **3a–c** were observed, i.e., no derivatives of **2** or **3** with hydroxyls on the proximal ring could be detected. (As noted below, **2** was detected as a trace product in degradation of **1**.)

Figure 1 shows the yields of products obtained at 10% conversion of **1**–**3** under various conditions. The data are interpolated from multiple runs sampled at various low percentage conversions to be standardized to the 10% conversion. The relative errors of the yields are ≤10%.

An immediately striking feature of the data in Fig. 1 is that the mass balance accounted for by singly hydroxylated compounds for compound **1**, while still below 50%, is significantly greater than that for the other two, under all conditions. Conspicuously missing from all degradations of **1** at low conversion was compound **2**. Also not observed (in any reactions) were biphenyl or 4-phenylphenol.

In the photo-Fenton reactions, at conversions of at least 10%, HPLC analysis of the reaction mixtures revealed many smaller peaks of higher polarity (as judged by chromatography) than any of the compounds in Chart 1. As mentioned previously, the rate of degradation of **1c** was determined under photo-Fenton conditions to observe if the degradation rates were correlated simply to the existence of the hydroxyl group. Its degradation rate was 0.8 μM/min, similar to that of **1**. Based on overall electron demand alone, this result is counterintuitive. It shows that the rate of degradation is sensitive to the relative position of the substituents and is at least consistent with the iron chelation hypothesis to explain the relative rates of degradation of **1**–**3**. Regardless, it became clear that the low overall mass balance was not a hindrance in interpreting the relative product distributions of the distal hydroxylations. Whatever other reactions occur in parallel with the distal hydroxylations, they do not interfere with the relative ratios of the **a**–**c** derivatives among themselves. Analysis at low conversion also ensures that secondary reactions have not grossly disturbed the initial product distributions.

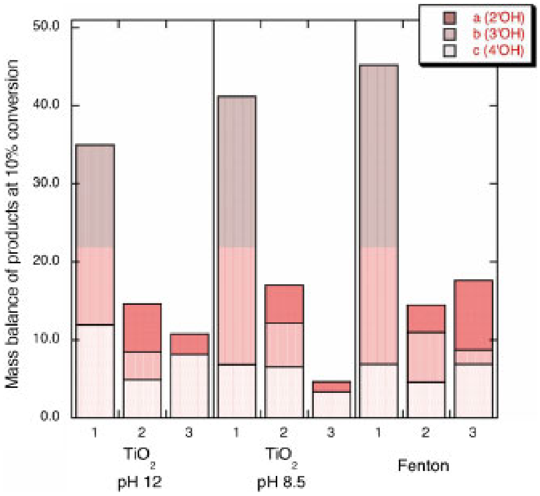


Figure 1. Product distributions and mass balance of singly hydroxylated products for degradation of **1**–**3** for photo-Fenton reactions and TiO_2 reactions at pH 12 and 8.5 at 10% conversion of starting material. The initial concentration of **1**, **2**, or **3** was 250 μm. The photo-Fenton reactions were carried out at pH 8.5.

The regioselectivity among the distal hydroxylation products for treatment of **1**–**3** can be interpreted using rules of thumb from electrophilic reactions of benzenes. Despite the near-neutral pH, the '4-carboxyphenyl' substituent clearly acts as a slightly electron-withdrawing group, favoring the meta-hydroxylation position in the reaction of **1**. The *meta:para* selectivity is a little <3:1 after accounting for the number of hydrogens (We presume sterics account for the lack of observation of **1a**, but acknowledge that some *ortho* hydroxylation is observed for the other two compounds.) This modest selectivity is consistent with that observed for many weak electron-withdrawing groups for electrophilic reactions of benzene, i.e., it is not the expectation that *meta* functionalization should be the exclusive result.

Given the more rapid initial degradation of molecules **2** and **3** under Fenton conditions, we presume that the qualitative *o*–*m*–*p* distributions are also meaningful. Addition of the 2-OH group to make compound **2** should have the effect of making the phenyl group slightly more electron donating than with the carboxyl group alone, thus somewhat negating its effect as an electron-withdrawing group. Indeed, the selectivity for formation of the *meta* product **2b** is quite low. Particularly pleasing from an esthetic standpoint, however, is the contrast between compounds **2b** and **c**. By reversing the alignment of the OH and carboxyl groups with compound **3**, the HO group is placed in conjugation to the distal phenyl, presumably greatly increasing its effective electron donation ability to the distal ring. Indeed, although **3b** is still observed, it is clear that the proximal phenyl acts as a mild *o:p* director for hydroxylation of the distal phenyl.

TiO_2-MEDIATED HYDROXYLATIONS

In contrast to the results with the photo-Fenton chemistry, the rates of degradation for compounds **1**–**3** were quite comparable to one another, both at pH 8.5 and 12. The simplest explanation for this is that the rate of degradation depends in very large part on the adsorption of the compound to the catalyst, and that this is dominated by the carboxylate functionality, common to all three compounds. Again, a rate check of a representative primary product was performed: **1c** was degraded at 8.4 ± 0.7 μM/min at pH 12, slightly slower than the other compounds.

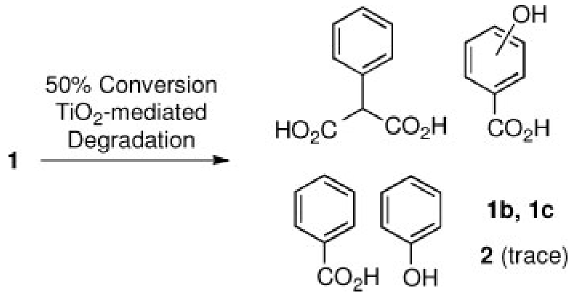
The hydroxylation product distributions and mass balances obtained for the TiO_2-mediated degradations were qualitatively similar to those obtained with the photo-Fenton reactions, but differed quantitatively in the following ways:

(1) For **1**, a slightly lower mass balance was obtained, but it was still greater than for the other two compounds. The selectivity for hydroxylation favored the *meta* position still, but to a slightly smaller degree.
(2) For **2**, the mass balance remained essentially unchanged, but again, somewhat more *ortho* and *para* hydroxylation is observed with TiO_2 than with photo-Fenton.
(3) For **3**, no *meta* product is observed at all and *para*-hydroxylation predominates to a greater extent over *ortho*.

In other words, the same pattern is observed with respect to *ortho/para versus meta* direction using TiO_2 and photo-Fenton, but the overall effect is slightly more biased toward *ortho/para* functionalization.

These results are consistent with the notion that the hydroxylation is also taking place with a hydroxyl-like species, but that the adsorption of the carboxylate to the TiO_2 makes it an effectively less electron-withdrawing substituent. Electron transfer mechanisms, i.e., attack of water on, for example, adsorbed $\mathbf{1}^{\bullet +}$, cannot be ruled out, however as water attack on the radical cation results in the same product. (e.g. Refs. [49–51] and references contained within, which address the oxidation of phenol.)

Degradations of **1** were carried out to higher conversion (approximately 50%) to try to identify some of the HPLC peaks that (as in the photo-Fenton chemistry) corresponded to downstream oxidation products. Instead of HPLC analysis, the reactions were lyophilized and exhaustively silylated and then subjected to GC-MS analysis. In addition to **1b** and **c**, a trace of **2** was observed, direct evidence of chemistry on the proximal phenyl group. Furthermore, phenylmalonic acid (phenylpropanedioic acid), benzoic acid, and phenol were also observed.



These latter compounds clearly represent multiple steps of degradation, *all* of which occur on the proximal phenyl, or what remains of it. Again, no 4-phenylphenol was observed in previous studies of the degradation of benzoic acid and its hydroxylated derivatives under TiO_2 conditions, up to three hydroxylations of benzene were observed (and extensive ring-opened products were not identified) and phenol was a very minor product at best.[41,52] Nonetheless, these compounds clearly indicate that reactivity can and does occur at the proximal phenyl and that once oxidation begins there, it continues more rapidly than reactivity at the distal phenyl. This is consistent with previous findings[28,29] showing that degradative electron transfer reactions typically become more facile as the ring is oxygenated.

CONCLUSIONS

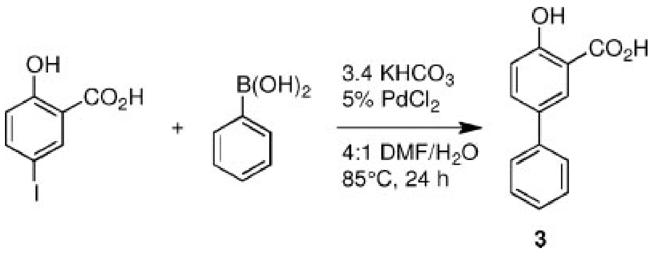
Ultimately, it must be concluded that compounds **1–3** are not especially good probes for distinguishing hydroxyl-like chemistry from single-electron transfer chemistry on TiO_2 surfaces. Although it seems clear that there is surface involvement in their primary chemistry (given the nearly identical rates), there is no particular evidence for specific SET-derived products not available through hydroxylation pathways or vice versa. The relative dearth of interpretable intermediates low mass balances present another difficulty, in that there is chemistry to which our methods are blind.

Nonetheless, the results reported here surely strengthen the assertion that selectivity in radical-based aromatic hydroxylation under both authentic hydroxyl radical chemistry (photo-Fenton) and TiO_2-mediated conditions can be thought of in terms of a nucleophilic benzene and electrophilic oxidizing agent. Although the biphenyls surely exist with a substantial twist between their π planes, some electronic communication between the rings is expected, and the carboxylic acid acts as a modest electron-withdrawing group. The dramatically different selectivity in hydroxylation of **2** (low selectivity, includes *meta*) and **3** (where the proximal phenyl clearly acts as an *ortho/para* director) surely demonstrates a subtlety in selectivity that requires this explanation.

EXPERIMENTAL

Materials

Compounds **1**, **1c** (Scheme 1), 4-iodobenzoic acid, 4- and 5-iodosalicylic acid, and the phenylboronic acids were used as obtained from commercial sources. Compounds **2** and **3** were prepared via Suzuki-Miyaura coupling using Larock's method,[53] as illustrated in Scheme 1 for compound **3**. The hydroxylated products shown in Chart 1 were prepared in two steps. First, the



Scheme 1. Suzuki-Miyaura coupling to prepare **3**.

aldehyde homolog was prepared in the same manner as **2** and **3**; it was then oxidized to the phenol and formic acid under Baeyer-Villiger conditions with *m*-CPBA.[54] Synthetic details are given in the Supporting Information. TiO_2 (Degussa P25) was used as received.

Photolyses

The standard suspensions for photocatalytic reactions were prepared to result in 100 mg of TiO_2 per 100 ml of deionized water. To 75 ml of water was added 100 mg of P25 TiO_2. Sonication for 5 min was used to break up larger aggregates of TiO_2. As noted, the pH was adjusted to 12.0 ± 0.5 or 8.5 ± 0.5 by adding 0.1 M NaOH at the start of the reaction and also throughout the reaction as needed to maintain that value. The substrate was added as a 25 ml aliquot from a 1 mM solution of the carboxylate in water to give a final concentration of 250 μm starting material. The mixture was then purged with O_2 and stirred for 30 min in the dark before the irradiation was started. Both stirring and O_2 purging were continued throughout the reaction. Ferrioxalate actinometry[55,56] was used to ensure photon flux remained constant and, in a few instances, to normalize rates to the rest of the data.

Photolyses were carried out with stirring at ambient temperature using a modified Rayonet mini-reactor equipped with a fan and 2 × 4-Watt broadly-emitting 350 nm 'black light' fluorescent tubes unless otherwise noted. Reaction times were dependent on the degree of degradation required, although 25 min was used for kinetic runs.

After appropriate irradiation times, samples were removed and acidified by addition of Amberlite IR-120 ion exchange resin. The TiO_2 and resin were separated by centrifugation, followed by filtration through a syringe-mounted 0.2 μm PES filter. Sample sizes were 1 ml for kinetics or 50 ml for product studies. The latter, larger samples were concentrated by rotary evaporation to approximately 2 ml and the residual water was removed by lyophilization.

For GC-MS product studies, lyophilized 50 ml samples were exhaustively silylated by treatment with 1 ml of anhydrous pyridine, 0.2 ml of 1,1,1,3,3,3-hexamethyldisilazane and 0.1 ml of chlorotrimethylsilane.[57] Samples were vigorously shaken for 1 min, and allowed to stand 5 min at ambient temperature. The resulting pyridinium chloride precipitate was separated by centrifugation prior to chromatographic analysis.

GC-MS work was done with a standard 25 m DB-5 (5% phenyl) column for chromatography, coupled to a time-of-flight mass spectral detector. The temperature program was 130 °C for 2 min, followed by a ramp to 280 °C at 20 °C/min. Routine work was done on another instrument with an FID detector.

Kinetic data were obtained using HPLC (diode array UV/Vis detection) analysis of 1 ml aliquots that were acidified with Amberlite and centrifuged before injection. A standard C18 reverse-phase column was used. The eluent was a 50:50 mixture of water and acetonitrile that contained 0.1% acetic acid. The flow was 1.0 ml/min.

Photo-Fenton reactions were set up as 100 ml solutions using 25 ml of the organic probe from a 1 mM stock solution, 10 ml of a solution containing 0.05 mM Fe^{3+} (as 0.0277 g $Fe_2(SO_4)_3$ in dilute H_2SO_4), and 1 ml (92 mM) of 30% H_2O_2. The pH was adjusted to 8.5. A rayonet lamp using 2 × 350 nm lamps was employed for photolysis. Aliquots were taken at regular time points with a crystal of sodium thiosulfate added to quench excess H_2O_2. These samples were directly injected into the HPLC for identification and quantification.

Acknowledgements

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