**Photodecomposition of tetrabromobisphenol A in aqueous humic acid suspension
by irradiation with light of various wavelengths**

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ABSTRACT

The reactive species generated in aqueous 3,3',5,5'-tetrabromobisphenol A (TBBPA)/humic acid (HA) suspensions above the TBBPA p*K*_a (~7.4), under various light-irradiation conditions, namely ambient and ultraviolet light, were investigated using electron paramagnetic resonance (EPR) spectroscopy and liquid chromatography-mass spectrometry (LC-MS). We confirmed that singlet oxygen and OH radicals are the key reactive oxygen species generated at wavelengths greater than 400 and 300 nm, respectively. The amount of 2,6-dibromo-*p*-benzosemiquinone anion radicals (2,6-DBSQ^{•-}) formed under irradiation at 400 nm increased linearly with respect to irradiation time; the initial reaction rate was $7.03 \times 10^{-9} \text{ mol g}^{-1} \text{ HA s}^{-1}$. The rate increased with increasing pH and light intensity. LC-MS and EPR spectroscopy showed that tribromohydroxybisphenol A was formed under irradiation at 300 nm via reaction of OH radicals with TBBPA. This study, for the first time, shows that the main byproducts formed during irradiation at wavelengths above 300 nm are 2,6-DBSQ^{•-} and tribromohydroxybisphenol A, generated from singlet oxygen (¹O₂) and OH radicals, respectively. Photodecomposition of TBBPA in the environment may occur by formation of ¹O₂ and OH radicals.

Keywords: Tetrabromobisphenol A; Humic acid; Photodecomposition; Electron paramagnetic resonance; 2,6-Dibromo-*p*-benzosemiquinone radical; Tribromohydroxybisphenol A

1. Introduction

Brominated flame retardants (BFRs) are extensively used in many consumer goods, ranging from fabrics to plastics and electronics (Alaee et al., 2003; Barontini et al., 2004; Reistad et al., 2005). The BFR with the highest global production is TBBPA. It is the most widely used BFR (about 50% of BFRs in current use) (BSEF, 2003; Hornung et al., 2003); its global annual use is 130 000 tons, with

more than 86% of the total in 2002 being used in Asia (BSEF, 2004). Fackler (1989) performed biodegradation studies in several media, e.g., soils, river sediments, and water, and showed that the TBBPA half-life is approximately 2 months. In contrast, no degradation was observed in sludge under sewage treatment conditions (Anonymous, 1992). Because TBBPA may bioaccumulate, it is potentially an environmental health problem (Berger et al., 2004; Morris et al., 2004; Thomsen et al., 2001; Watanabe and Sakai, 2003). Environmental photochemical transformations of TBBPA can occur in the atmosphere and in surface waters. The absorption spectra of the unionized and dissociated forms of TBBPA are very different (Richard and Grabner, 1999), which shows that the rate of TBBPA photodecomposition is pH dependent. Humic acid (HA) plays a number of important roles in the environment, including controlling the pH balance, governing the mobility of contaminants through absorption, aggregation, and sedimentation, and metal chelation (Kim and Corapcioglu, 2002; McCarthy et al., 1998; Warwick et al., 2000). Several reported studies of the photochemistry of HA in the environment suggest that HA acts as a sensitizer or precursor for the production of reactive intermediates, including $^1\text{O}_2$, superoxide anion radicals ($\bullet\text{O}_2^-$), and H_2O_2 in oxygenated natural waters (Aguer et al., 2005; Canonica et al., 1995; Cooper and Zika, 1983; Polewski et al., 2005; Wilson et al., 2000). Radical reactions are thought to be responsible for the formation of the intermediates in TBBPA decomposition pathways. We previously reported that at pH values at or above its pK_a (~ 7.4), TBBPA is rapidly oxidized by $^1\text{O}_2$ generated by rose bengal (RB) or methylene blue (Han et al., 2008). In aqueous alkaline solutions, TBBPA is a very efficient $^1\text{O}_2$ quencher ($k_q = 1.44 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and even at neutral pH, at which TBBPA is only partly dissociated, the rate constant is high ($k_q = 3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). We also previously suggested that the main photoproduct generated from TBBPA dissolved in HA is the 2,6-DBSQ $^{\bullet-}$ (Han et al., 2009). However, information on the photochemical properties of TBBPA in the presence of HA is very limited, although the main intermediate formed by TBBPA photodecomposition has been identified

as 2,6-DBSQ^{•-}.

The solar radiation that reaches the Earth's surface is limited to wavelengths above 290 nm and generally cannot directly promote organic compound photolysis in the absence of photocatalysts such as HA. Previous studies of TBBPA decomposition and its intermediates have mainly focused on a single light-irradiation condition (Eriksson et al., 2004; Horikoshi et al., 2008; Katayama-Hirayama et al., 2014; Xu et al., 2011).

Quantitative analysis of the radical reactions that occur on irradiation of TBBPA dissolved in HA and identification of the products generated by these radical reactions under various light-irradiation conditions, namely ambient (400 nm) and ultraviolet (300 nm) light, are therefore of interest.

In this study, our aim was to investigate the behaviors of reactive species generated by photosensitized degradation of TBBPA dissolved in HA, and their quantitative analysis using EPR spectroscopy and LC-MS. The reactive oxygen species and photoproducts were investigated to elucidate the TBBPA photolysis mechanism.

2. Materials and methods

2.1. Materials

HA, sodium azide, acetonitrile, diphenyl-2-picrylhydrazyl (DPPH), Triton X-100, catalase (CAT), superoxide dismutase (SOD), ascorbic acid, *o*-phenanthroline, and potassium chromate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). TBBPA (98% purity) was purchased from Tokyo Chemical Industries. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was purchased from the Labotech Co. (Tokyo, Japan); it was vacuum distilled and stored at -70 °C. All other chemicals were reagent grade or better. All measurements were performed at room temperature. Buffers were prepared using compounds of reagent grade or better. The pH was measured using a glass electrode. The HA contains free and bound phenolic OH groups, nitrogen and oxygen as

bridging units, and COOH groups at various positions on aromatic rings.

2.2. Methods

All solutions were prepared with distilled water obtained using a water purification system (Mill-Q, Millipore). The solutions were prepared by adding 10 mM phosphate buffer and adjusting to the desired pH with NaOH or HCl. A stock solution of HA of concentration 50 mg mL⁻¹ was prepared. This was diluted to the desired concentration with pH 9.0 phosphate buffer. All EPR experiments were conducted in a 2.0 mL clear Teflon tube, with continuous stirring at a constant speed for 10 s to ensure complete mixing to achieve uniform distribution and full suspension of the HA. LC-MS experiments were performed in the presence and absence of sodium azide (20 mM) as an ¹O₂ scavenger. In each experiment, TBBPA (1.0 mM) and HA (1.0 mg mL⁻¹) were added to pH 9.0 phosphate buffer in a 10 mL clear glass vial. The mixture in the vial was continuously stirred at a constant speed for 10 s to ensure complete mixing to achieve uniform distribution and full suspension of the HA. The mixture was then irradiated using a USHIO Optical Mudulex 0.25 kW Hg lamp (Tokyo, Japan). The distance between the lamp and the solution was 30 cm. The presented concentrations were final values. All samples were prepared in the dark (below 50 lx, 0.8 W m⁻²), The ambient and visible-light conditions were 2.8 and 950 W m⁻², respectively. The rate constant (*k*) represents the generation rate of 2,6-DBSQ⁻. The ferric ion concentration in the HA solution was determined by a phenanthroline spectrophotometric method (Fortune and Mellon, 1938) using a UV-visible spectrophotometer (Shimadzu, UV-2550). For determination of the ferric ion concentration in the HA solution, ascorbic acid solution (to reduce Fe³⁺ to Fe²⁺) and phenanthroline solution were added to the pH 9.0 buffer solution. The Fe²⁺ absorbance was measured at 510 nm; the detection limit was 5.0 × 10⁻⁶ M.

Han et al. (2009) reported that ¹O₂ was generated from HA (1.0 mg mL⁻¹) solution under ambient conditions. The amount generated increased with increasing pH above pH 8.0; at alkaline pH,

TBBPA has an absorption maximum at 320 nm. Han et al. (2008) also reported that 2,6-DBSQ^{•-} was generated under visible light ($\lambda > 400$ nm) from a solution containing TBBPA (1.0 mM) and RB (20 μ M). We therefore used the conditions pH 9.0, HA concentration 1.0 mg mL⁻¹, and TBBPA concentration 1.0 mM in this study.

2.3. EPR measurements

EPR spectra were recorded using a JEOL JES-1x EPR spectrometer (Tokyo, Japan), operated at 10 mW (9.43 kHz) with G modulation amplitude and 100 kHz modulation frequency. Samples (40 μ L) were placed in quartz flat cells of total capacity 100 μ L and irradiated directly inside the microwave cavity of the spectrometer using a USHIO Optical Mudulex 0.25-kW Hg lamp (Tokyo, Japan). Radiation from the lamp was passed through a glass window ($\lambda > 300$ nm) or a 30 mm path-length liquid filter ($\lambda > 400$ nm; aqueous solution containing NaNO₂ 48.4, Na₂CO₃ 1.0, and K₂CrO₄ 0.2 g L⁻¹) to remove wavelengths below 400 nm, and the irradiated samples were used for EPR spectroscopy and LC-MS.

The sample was exposed to ambient light radiation using a typical cool white fluorescent lamp (FHF32EX-N-K, Hitachi, Japan), which emits in the visible spectrum at wavelengths between 400 and 700 nm. The sample was placed 1.5 m below a set of two fluorescent lamps, which were fitted with open reflectors. The light intensity on the sample was 700–750 lx, 2.78 W m⁻². All solutions were prepared using distilled water (Mill-Q, Millipore). The distilled water was treated with Triton X-100 before use.

Hyperfine coupling constants (hfcs) were obtained by accumulating, simulating, and optimizing spectra using software installed on a DELL computer, as described elsewhere (Duling et al., 1994). The radical concentration was calculated by comparing the signal intensity with that of a standard solution of DPPH; the *g* value was calculated based on those of Mn²⁺ and DPPH.

In EPR experiments, the g value gives information on a paramagnetic center's electronic structure, and a_{2H} and a_H are the hfcs of the electrons of hydrogen nuclei and are directly related to the spectral line spacing.

2.4. LC-MS measurements

The samples were filtered using a 0.4- μ m filter and placed in a clear glass vial of total capacity 5 mL. After irradiation with the Hg lamp, the TBBPA photoproducts were analyzed using an LC-MS-ion trap-time-of-flight system (Shimadzu, Kyoto, Japan) with a reverse-phase column (ODS-80Ts QA, 2.0 $\times$ 150 mm, 5 μ m, Tosoh, Tokyo, Japan). The mobile phase was water (solvent A) and acetonitrile (solvent B). Before sample injection, the column was equilibrated with A:B = 85:15 (v/v). The time program for solvent B (vol% in solvent A) was as follows: 0 to 30 min, gradient 15% to 90%; 30 to 60 min, 90%; 60 to 80 min, 100%. The flow rate and column temperature were maintained at 0.2 mL min⁻¹ and 40 °C, respectively, throughout the procedure. The injection volume was 1 μ L. The entire effluent flow was directed into an electron-spray ionization source operated in positive and negative ion modes. The MS parameters were as follows: probe voltage, 4.5 kV (positive mode), -3.5 kV (negative mode); nebulizing gas flow, 1.5 L min⁻¹; block heater temperature, 200 °C; curved desolvation line temperature, 200 °C; ion accumulation time, 30 ms; scanning range, 200–2000 m/z . Data-dependent MS/MS spectra were obtained under the following conditions: collision-induced dissociation energy, 50%; collision gas, 50%; q value, 0.251 (45 kHz); ion accumulation time, 30 ms; scanning range, 100–1000 m/z .

3. Results and discussion

3.1. EPR spectra generated during irradiation with visible light ($\lambda > 400$ nm)

The EPR spectrum of aqueous TBBPA (1.0 mM) solution containing HA was obtained under visible-light conditions (Fig. 1A). The EPR signal of 2,6-DBSQ^{•-} was observed. Figure 1B shows

the base line of the EPR spectrum, obtained from a blank sample, i.e., free of HA. The 2,6-DBSQ^{•-} signal consists of a strong triplet of lines, with peak:height ratios of 1:2:1, with hyperfine constants $a_{2H} = 2.36$ G and $g = 2.0056$. The 2,6-DBSQ^{•-} signal disappeared on addition of sodium azide (Fig. 1C), confirming that its generation was essentially ¹O₂ dependent. These results are in agreement with previous reports of the 2,6-DBSQ^{•-} EPR signal generated by the reaction of ¹O₂ with TBBPA (Han et al., 2009, 2008). This confirms that 2,6-DBSQ^{•-} is one of the byproducts generated from the reaction of ¹O₂ with the TBBPA in our buffer solution.

3.2. Effect of HA concentration on 2,6-DBSQ^{•-} formation

Figure 2A shows the time course of 2,6-DBSQ^{•-} generation for various HA concentrations from 0.1 to 1.0 mg mL⁻¹. The amount of 2,6-DBSQ^{•-} formed increased linearly with irradiation time up to 480 s, for all HA concentrations. However, above 480 s, for the highest HA concentration (1.0 mg mL⁻¹), the rate of 2,6-DBSQ^{•-} formation increased according to a rectangular hyperbolic pattern (the amounts of 2,6-DBSQ^{•-} generated were 3.96 and 4.02 at 600 and 720 s, respectively). These results clearly show that the HA surface provides active reaction sites for the formation of stable 2,6-DBSQ^{•-}; the parabolic increase at the highest HA concentration occurs because addition of a fixed concentration of TBBPA, i.e., 1.0 mM, limits the reaction. A plot of the molar concentration of 2,6-DBSQ^{•-} versus the HA concentration was produced (Fig. 2B) based on the linear time range for the 2,6-DBSQ^{•-} formation rate for all HA concentrations, i.e., up to 480 s. A linear relationship was observed; the slope represents the 2,6-DBSQ^{•-} formation rate per unit mass of HA, i.e., 7.03×10^{-9} mol g⁻¹ HA s⁻¹. This reaction rate is about 20 times higher than that achieved with goethite, which acts as a natural sensitizer (Han et al., 2011).

3.3. Effect of pH on 2,6-DBSQ^{•-} formation

The solution pH affects the transformation of halogenated organic compounds, e.g., the solubility of TBBPA in water increases with pH (Choi and Hoffmann, 1997, 1995). Miyamoto et al. (2014)

reported that the efficiency of TBBPA degradation increased significantly above pH 8.0, and the debromination of TBBPA increased rapidly under alkaline conditions. We investigated the influence of pH on 2,6-DBSQ^{•-} formation in the degradation of TBBPA by irradiating TBBPA and HA in buffer solutions of pH 6.8, 7.4, 8.0, and 9.0. Figure 3A shows the time course of 2,6-DBSQ^{•-} generation for various pH ranges. The formation of 2,6-DBSQ^{•-} increased linearly with respect to a irradiation time up to 360 s in all pH ranges. Above 360 s, the amount of 2,6-DBSQ^{•-} formed reached a plateau. The initial generation rates of 2,6-DBSQ^{•-} were calculated to be 0.7, 2.4, 8.4, and $12.0 \times 10^{-9} \text{ M s}^{-1}$ at pH 6.8, 8.0, 9.0, and 10.0, respectively. Figure 3B shows that the reaction rate increased significantly with increasing pH at pH values higher than the compound pKa, whereas it did not greatly increase at pH values lower than the compound pKa. These results show that at pH values below its pKa, the quantum yield of TBBPA photodecomposition decreases with decreasing pH, whereas at pH values above its pKa, photodecomposition is independent of pH (Eriksson et al., 2004); they also show that the TBBPA degradation and debromination rates increase sharply with increasing pH at pH values higher than the compound pKa, as previously suggested by several researchers (Guo et al., 2012; Zhang et al., 2009; Miyamoto et al., 2014).

3.4. Effect of irradiation intensity on 2,6-DBSQ^{•-} generation rate

Figure 4 shows the effect of the irradiation intensity on the rate of 2,6-DBSQ^{•-} generation under ambient- (2.8 W m^{-2}) and visible-light (950 W m^{-2}) conditions. The increase in the 2,6-DBSQ^{•-} generation rate constant during irradiation with visible light was greater than that under ambient light. The rate constants were calculated to be 8.4×10^{-9} and $0.24 \times 10^{-9} \text{ M s}^{-1}$ for visible and ambient light, respectively; no 2,6-DBSQ^{•-} was generated under dark conditions (0.8 W m^{-2}). The 2,6-DBSQ^{•-} generation rate increased with increasing irradiation intensity (data not shown).

3.5. EPR spectra generated during irradiation with UV light ($\lambda > 300 \text{ nm}$)

Figure 5A shows that the EPR spectrum obtained during irradiation ($\lambda > 300 \text{ nm}$) of TBBPA and

HA in alkaline buffer (pH 9.0) consisted of a triplet signal and a doublet signal. A simulated spectrum and the values of the splitting constants are shown in Fig. 5B. The empty circles mark the triplet, which has intensity ratios of 1:2:1, $a_{2H} = 2.36$ G, and $g = 2.0056$ (55% of the total EPR intensity). These parameters are in accord with those for 2,6-DBSQ $^{\bullet-}$, observed under visible-light conditions. The doublet has $a_H = 3.90$ G and $g = 2.0048$ (45%). The intensity of the $g = 2.0048$ radical did not decrease, but the 2,6-DBSQ $^{\bullet-}$ signal disappeared, on addition of sodium azide (Fig. 5C). These results indicate that the doublet signal did not arise from 1O_2 generated during UV irradiation of TBBPA in the presence of HA in alkaline buffer (pH 9.0).

Several reports have shown that organic compounds containing a phenyl ring effectively quench free radicals such as 1O_2 , $\bullet O_2^-$, and OH radicals (Carlos et al., 2013; Francisca et al., 2013; Kumuda and Chandan, 2002), and HA enhances the quenching effect under various irradiation conditions (Gray and Lawrence, 1995; Junfeng et al., 2013; Zeng et al., 2003).

Some researchers have reported that $HO_2\bullet$ was generated from solutions containing ferric ions on irradiation with UV-A light (Kiwi et al., 1993; Ruch and Bielski, 1985); $HO_2\bullet$ reacts with Fe^{2+} to form H_2O_2 (equation 1), inducing a Fenton reaction, which generates, $\bullet OH$ (equation 2):

A hybrid reaction involving Fe^{2+} and UV-A light could therefore generate OH radicals. A trace amount of ferric ions was present in the HA solution used in this experiment (data not shown).

To investigate this possibility, we irradiated TBBPA and HA in alkaline buffer solution after the addition of an OH radical spin trap, i.e., DMPO, or SOD and CAT to scavenge $\bullet O_2^-$, under UV light. As shown in Fig. 6A, a weak EPR signal consisting of four lines with intensity ratios of 1:2:2:1

(filled triangles) was observed, with $a_N = 14.9$ G, $a_H = 14.9$ G, and $g = 0055$. This signal was identified as that from DMPO–OH, i.e., the OH radical adduct of DMPO. The doublet signal in the spectrum disappeared after addition of 100 U mL^{-1} SOD and 1300 U mL^{-1} CAT (Fig. 6B). This doublet was not observed when DMPO alone was irradiated with intense UV light (data not shown).

These results suggest that OH radicals are generated during UV irradiation of TBBPA in the presence of HA.

3.6. Photoproducts generated during irradiation with UV light ($\lambda > 300 \text{ nm}$)

Several reports have suggested that byproducts such as 4-cyclopropenyl-2,6-dibromophenol, 2,6-dibromophenol, 2,6-dibromo-4-(propan-2-ylidene)cyclohexa-2,5-dienone, and phenol are formed by the reactions of free radicals generated during irradiation of TBBPA in aqueous solution (Fukushima et al., 2010; Guo et al., 2014; Li et al., 2014).

In previous studies of TBBPA oxidation (Eriksson et al., 2004; Lin et al., 2009), 2,6-dibromo-4-isopropenylphenol radicals were found to be one of the main intermediates, and 2,6-DBSQ $^{\bullet-}$ was also detected as a major byproduct.

We used LC-MS to identify the photoproducts of TBBPA in alkaline buffer (pH 9.0) under various reaction conditions. Figure 7 shows a chromatogram of the irradiated buffer solution containing TBBPA and HA over 5 min. Three photoproducts (X, Y, and Z, Fig. 7) were detected in the irradiated solution. The insets show the mass spectra for photoproducts X, Y, and Z. The m/z values for compounds X and Y were 292.9022 (calcd. m/z 292.9000), obtained in positive mode, and 308.8928 (calcd. m/z 308.8954), obtained in negative mode, respectively, and they were identified as the 2,6-dibromo-4-isopropenylphenol radical, 2,6-dibromobenzosemiquinone, and 2,6-dibromo-4-(2-hydroxypropan-2-yl)phenol, based on the bromine isotopic pattern. The MS peak of product X was not obtained, suggesting the semiquinone radical form. However, these signals disappeared on addition of sodium azide as a $^1\text{O}_2$ scavenger, as shown in Fig. 7B. These results are in

good agreement with the EPR spectra reported by Han et al. (Han et al., 2008). These compounds are formed from singlet oxygen. The m/z value for the photoproduct Z was 478.8312 (calcd. m/z 478.8321), and Z was identified as tribromohydroxybisphenol A. As shown in Fig. 8B, this signal did not disappear on addition of sodium azide. The results shown in Fig. 6 and 7 suggest this compound is formed from OH radicals rather than from $^1\text{O}_2$.

We are currently studying the photodegradation of TBBPA in the presence of HA under solar light and have detected tribromohydroxybisphenol A with a doublet signal from OH radicals, and 2,6-DBSQ $^{\bullet-}$ generated from $^1\text{O}_2$ (unpublished data).

Our results suggest that TBBPA degradation in the environment may be the result of reactions with photochemically generated reactive species such as singlet oxygen and OH radicals.

4. Conclusions

This study shows that various radicals can be generated in TBBPA/HA mixtures during irradiation by different light sources. Under UV-visible irradiation, photodecomposition is based on photogeneration of $^1\text{O}_2$, and 2,6-DBSQ $^{\bullet-}$ is formed by the reaction of singlet oxygen with TBBPA. The amount of 2,6-DBSQ $^{\bullet-}$ formed increases with increasing HA concentration and pH, and is light-intensity-dependent under alkaline conditions. Under irradiation with UV-A or sunlight, tribromohydroxybisphenol A is formed via the reaction of OH radicals with TBBPA. In irradiation of TBBPA/HA with sunlight containing a few per cent UV-A radiation, OH radicals and $^1\text{O}_2$ are both key reactive oxygen species.

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List of Figures

Fig. 1. EPR spectra of 1.0 mM TBBPA in presence (A) and absence (B) of HA suspension (1.0 mg mL⁻¹) during irradiation (pH 9, 5 min, $\lambda > 400$ nm); spectrum of mixture in A in presence of sodium azide (20 mM, pH 9.0) (C). Triplet signal is marked with empty circles ($a_{2H} = 2.36$ G, $g = 2.0056$). EPR spectra were recorded at room temperature, using an EPR spectrometer, with 10 mW microwave irradiation (9.438 GHz) and 0.063 mT field modulation (100 kHz). Visible-light condition was 950 W m⁻².

Fig. 2. Time course of 2,6-dibromo-*p*-semiquinone radical generation for HA concentrations from 0.1 to 1.0 mg mL⁻¹ (TBBPA 1.0 mM, pH 9.0) on irradiation ($\lambda > 400$ nm). Data in inset in (A) are 2,6-dibromo-*p*-semiquinone radical formation rates at four HA concentrations (0.1, 0.25, 0.5, and 1.0 mg mL⁻¹). (B) shows data in (A) replotted, showing amount of 2,6-dibromo-*p*-semiquinone radicals accumulated up to 480 s of irradiation time versus HA concentration. The amount of 2,6-dibromo-*p*-semiquinone radicals was determined as described in Materials and methods. Results are mean $\pm$ standard deviation ($n = 4$). EPR spectra were recorded at room temperature, using an EPR spectrometer, with 10 mW microwave irradiation (9.438 GHz) and 0.063 mT field modulation (100 kHz). Visible-light condition was 950 W m⁻².

Fig. 3. Time course of 2,6-dibromo-*p*-semiquinone radical generation at various pH values (TBBPA 1.0 mM, HA 1.0 mg mL⁻¹, pH 9.0) on irradiation ($\lambda > 400$ nm). Data in inset in (A) are 2,6-dibromo-*p*-semiquinone radical formation rates at four pH concentrations (pH 6.8, 8.0, 9.0, and 10.0). (B) shows data in (A) replotted, showing amount of 2,6-dibromo-*p*-semiquinone radicals accumulated up to 360 s of irradiation time versus pH. The amount of 2,6-dibromo-*p*-semiquinone radicals was determined as described in Materials and methods. Results are mean $\pm$ standard deviation ($n = 4$). EPR spectra were recorded at room temperature, using an EPR spectrometer, with 10 mW microwave irradiation (9.438 GHz) and 0.063 mT field modulation (100 kHz). Visible-light condition was 950 W m⁻².

Fig. 4. Comparison of generation rates of 2,6-dibromo-*p*-semiquinone radicals under ambient and visible light (TBBPA 1.0 mM, HA 1.0 mg mL⁻¹, pH 9.0). Filled circles represent irradiation with visible light ($\lambda > 400$ nm), and filled squares are irradiation with ambient light. Filled triangles represent dark conditions. The ambient and visible-light conditions were 2.8 and 980 W m⁻², respectively. The amount of 2,6-dibromo-*p*-semiquinone radicals was determined as described in Materials and methods. Results are mean $\pm$ standard deviation ($n = 4$). EPR spectra were recorded at

room temperature, using an EPR spectrometer, with 10 mW microwave irradiation (9.438 GHz) and 0.063 mT field modulation (100 kHz).

Fig. 6. EPR spectrum generated in presence of HA suspension (1.0 mg mL^{-1}) with 1.0 mM TBBPA (pH 9) (A) during irradiation (5 min, $\lambda > 300 \text{ nm}$), simulation (B) of spectrum A, and spectrum of solution in (A) in presence of sodium azide (20 mM, pH 9.0) (C). Triplet signals in spectrum A and B are marked with empty circles ($\circ$, $a_{2H} = 2.36 \text{ G}$, $g = 2.0056$, 55%). Doublet signals in spectrum A, B, and C are marked with filled circles ($\bullet$, $a_H = 3.90 \text{ G}$, $g = 2.0048$, 45%). EPR spectra were recorded at room temperature, using an EPR spectrometer, with 10 mW microwave irradiation (9.438 GHz) and 0.063 mT field modulation (100 kHz).

Fig. 7. LC-MS chromatograms of 1.0 mM TBBPA in presence of HA suspension (1.0 mg mL^{-1}) (A, pH 9.0) during irradiation (5 min, $\lambda > 300 \text{ nm}$), and in presence of sodium azide (20 mM) (B). Insets show mass spectra of byproducts X (positive), Y (negative), and Z (negative), corresponding to retention times. LC-MS chromatograms were recorded as described in Materials and methods.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Graphical Abstract