# Why Dissolved Organic Matter Enhances Photodegradation of Methylmercury

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S *Supporting Information*

ABSTRACT: Methylmercury (MeHg) is known to degrade photochemically, but it remains unclear what roles naturally dissolved organic matter (DOM) and complexing organic ligands play in MeHg photodegradation. Here we investigate the rates and mechanisms of MeHg photodegradation using DOM with varying oxidation states and origins as well as organic ligands with known molecular structures. All DOM and organic ligands increased the rate of MeHg photodegradation under solar irradiation, but the first-order rate constants varied depending on the oxidation state of DOM and the type and concentration of the ligands. Reduced DOM photochemically degraded MeHg 3 times faster than oxidized DOM. Compounds containing both thiol and aromatic moieties within the same molecule (e.g., thiosalicylate and reduced DOM) increased MeHg photodegradation rates far more than those containing only aromatics or thiols (e.g., salicylate or glutathione, or their combinations). The mechanism is attributed in part to strong binding between MeHg and thiolates that resulted in direct energy transfer from excited triplet state of the aromatics to break the Hg−C bond in MeHg. Our results suggest that, among other factors, the synergistic effects of thiol and aromatics in DOM greatly enhance MeHg photodegradation.
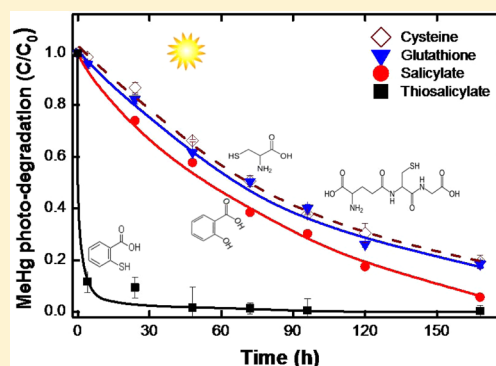
INTRODUCTION

Monomethylmercury (MeHg) has been studied extensively with regard to its environmental fate and transformation because of its potent neurotoxicity and bioaccumulation in the food web.[1−6] Both biotic and abiotic processes can break down MeHg,[7−9] but photochemical degradation is considered a major sink for MeHg and is responsible for as much as 80% of demethylation in some freshwater lakes.[10−13] Studies have shown that ultraviolet (UV) radiation under natural sunlight primarily drives the photolysis of MeHg in surface waters,[5,6,14,15] but the reaction mechanism remains poorly known, especially regarding the roles of dissolved organic matter (DOM) and complexing organic ligands in MeHg photodegradation. There is currently a lack of consensus regarding how and if DOM is involved in the photolysis of MeHg.[5,6,16,17] Several studies reported a positive correlation between MeHg photodegradation and DOM concentration,[6,11,16,17] but others found no significant influence of DOM on photodegradation.[5,12] For example, labile iron, not DOM, and reactive oxygen species (ROS, such as hydroxyl radical, •OH) were shown to be important in MeHg photodegradation.[12] Other studies[17] found that MeHg photodegradation was greatly enhanced by DOM and that singlet oxygen ($^1O_2$) radicals, not •OH, were responsible. However, recent studies by Black et al.[5] and Tai et al.[16] found that none of these parameters alone ($^1O_2$, •OH, thiols, DOM, and iron concentrations) is effective in MeHg photodegradation. These authors suggest that multiple pathways[5] or direct photolysis of

MeHg−DOM complexes[16] may be involved. Fernandéz-Goméz et al.[6] proposed that the light spectrum dependent MeHg photolysis is due to a cocktail of different organic radicals and ROS that are present over a wide spectral range.

The differences observed in these previous studies illustrate important gaps in our understanding of the roles of DOM in MeHg photodegradation. Thus, the primary objective of this study is to determine the rates and mechanisms of MeHg photodegradation influenced by DOM. Several organic ligands with known molecular structures were selected as DOM analogues in the study. We examined (1) the effects of two types of DOM (either aquatic or terrestrial) and oxidation states (either reduced or oxidized), (2) the chemical structure and functional groups (e.g., aromatics and thiols) of selected ligands, and (3) the roles of $^1O_2$ and •OH radicals and the excited triplet state of DOM ($^3DOM^*$) in MeHg photodegradation. We hypothesized that thiolate and aromatic moieties in DOM work synergistically, which results in strong MeHg−DOM binding and direct energy transfer from $^3DOM^*$ to break the Hg−C bond in MeHg.

MATERIALS AND METHODS

DOM Samples and Organic Ligands. Two DOM samples were used in this study; one was isolated from the

contaminated East Fork Poplar Creek (EFPC-DOM) in Oak Ridge, TN,[18] and the other was a reference Elliot soil humic acid (E-SHA) from the International Humic Substances Society.[19,20] They were used either in the oxidized or reduced state (by H_2/Pd reduction), as described previously.[20] Six organic ligands were used as DOM analogues,[17,21−23] including thiosalicylate and 6-thioguanine (aromatic thiols), salicylate (aromatic carboxyl), cysteine and glutathione (nonaromatic thiols), and acetate (nonaromatic carboxyl) (see Figure S1 of the Supporting Information for the chemical structure and UV−visible absorbance spectra). To minimize the oxidation of thiol compounds, reagent solutions were prepared in deoxygenated water and samples handled in an anaerobic chamber.[24]

Photodegradation Experiments. MeHg reactant solutions were prepared in 100 mL volumetric flasks by adding stock DOM or ligand solutions and then the MeHg stock, which was prepared freshly for every batch of the experiment from a certified standard [5 μM, in 0.2% HCl and 0.5% (v/v) acetic acid] from Brooks Rand Laboratories (Seattle, WA). Unless otherwise specified, the final MeHg concentration was 50 pM (with 0.87 μM acetate), the ligand concentration was 2 μM, and the DOM concentration was ∼0.13 mM DOC (dissolved organic carbon). All experiments were performed under low-ionic strength conditions (∼1 mM KCl), typically observed in natural freshwater,[25] and the pH was adjusted and maintained at 6.9 ± 0.1. For concentration-dependent studies, the final concentrations of thiosalicylate ranged from 0.1 nM to 2 μM and those of EFPC-DOM ranged from 0.01 to 0.13 mM DOC, equivalent to an estimated reactive thiol content of approximately 1−12.8 nM.[18,19] The reactant solutions (3 mL each) were then pipetted into a series of 4 mL clear borosilicate glass vials (Wheaton Industries) with a light transmission efficiency of >80% from 300 to 800 nm (Figure S2 of the Supporting Information). Control samples were prepared in the same way either without organic ligands or with organic ligands but in the dark (using amber glass vials wrapped with aluminum foil).

Photodegradation experiments were initiated by placing samples in a simulated solar chamber (Suntest XLS+) (see Figure S3 of the Supporting Information for the spectrum and additional information). The light irradiance was 40 W m^{-2} for UV (300−400 nm) and ∼373.6 W m^{-2} total (300−800 nm), typical midsummer conditions in eastern Tennessee (Figure S4a of the Supporting Information).[26,27] Under these conditions, similar rates of MeHg photodegradation were observed using either simulated or natural sunlight (Figure S4b of the Supporting Information). Two or three samples were analyzed for MeHg at selected times by modified EPA method 1630 (Supporting Information). Selected samples were also analyzed for total Hg (Supporting Information), and the recovery was usually within ±10%. The pseudo-first-order rate constant (k_d) of MeHg photodegradation was determined using eq 1:

$$\ln[\text{MeHg}]_t = \ln[\text{MeHg}]_0 - k_d t \tag{1}$$

where $[\text{MeHg}]_0$ is the initial MeHg concentration and $[\text{MeHg}]_t$ is the MeHg concentration at time t. To compare with the literature data, the photon flux-normalized degradation rate constant (k_{d-ph}, m^2 E^{-1}) was calculated on the basis of a total light irradiance of 373.6 W m^{-2} at the mean wavelength of 550 nm.[5,6,11,16]

To examine if ^{3}DOM*, $^1O_2$, or $^\bullet$OH radicals may be involved in MeHg photodegradation, experiments were performed in the presence of 10 mM isoprene (a triplet state quencher), 10 mM sodium azide (NaN$_3$, a $^1O_2$ quencher), or 0.01% (v/v) isopropyl alcohol (a $^\bullet$OH scavenger) as used in previous studies.[5,16,17] Salicylate (2 μM), thiosalicylate (5 nM), and reduced EFPC-DOM (0.13 mM DOC) were used in these experiments, and all other experimental conditions were identical to those described above.

■ RESULTS AND DISCUSSION

We first examined whether DOM enhances MeHg photodegradation in the presence of either reduced or oxidized EFPC-DOM or E-SHA. In all cases, addition of DOM increased the rate of photodegradation of MeHg, and the MeHg concentration decreased exponentially over time (Figure 1a). Approximately 90% MeHg was degraded in a week with the reduced DOM, whereas only 50−60% of MeHg was degraded with the oxidized DOM. The k_{d-ph} values (±standard deviation) for reduced and oxidized EFPC-DOM were (4.3 ± 0.3) × 10^{-3} and (1.4 ± 0.1) × 10^{-3} m^2 E^{-1}, respectively, and were (3.2 ± 0.2) × 10^{-3} and (1.0 ± 0.1) × 10^{-3} m^2 E^{-1} for reduced and oxidized E-SHA, respectively (Table S1 of the Supporting Information). These values were comparable to those reported for coastal seawater (3.2 × 10^{-3} m^2 E^{-1}) and for boreal lakes and wetlands (2−7.5 × 10^{-3} m^2 E^{-1}).[5,6] Controls without DOM (but with a 0.87 μM acetate background) and dark controls with DOM exhibited negligible MeHg degradation (<10%) (Figure 1a and Figure S5 of the Supporting Information), indicating that MeHg was degraded through photochemical reactions and DOM substantially enhanced the reaction. More importantly, the photodegradation rate was ∼3-fold higher with reduced DOM than with oxidized DOM (for both EFPC-DOM and E-SHA).

To understand why reduced DOM is more effective than oxidized DOM in enhancing MeHg photodegradation, we investigated several model organic ligands (2 μM each) and found that they increased the rate of MeHg photodegradation to varying degrees (Figure 1b). Thiosalicylate and 6-thioguanine (aromatic thiols) were the most effective in enhancing photodegradation, and the reaction was nearly complete within 1 h. A high k_{d-ph} value (0.27 ± 0.03 m^2 E^{-1}) was obtained for 6-thioguanine (Table S1 of the Supporting Information), but it was not determined for thiosalicylate because of limited data within the first hour. Under the same conditions, however, MeHg photodegradation was slower in the presence of salicylate (a nonthiol aromatic ligand), glutathione or cysteine (nonaromatic thiols), or a mixture of salicylate and glutathione, with k_{d-ph} varying slightly from (1.8 ± 0.1) × 10^{-3} to (3.0 ± 0.1) × 10^{-3} m^2 E^{-1}. As stated, acetate (0.87 μM) in the background had little influence on MeHg photodegradation (Figure 1a). These results indicate that the enhancement effects of organic ligands in MeHg photodegradation depend on the chemical and structural properties of the ligand, with the highest degradation rate observed for ligands containing both aromatic and thiol moieties in the same molecule. This is especially evident if we compare MeHg photodegradation by salicylate and thiosalicylate (Figure 1b). The only structural difference between these two compounds is that the former contains a −OH group and the later contains a −SH group at the β position of the benzene ring. The presence of the −SH group on thiosalicylate (similarly on 6-thioguanine) resulted in a k_{d-ph} value at least 1 order of magnitude higher
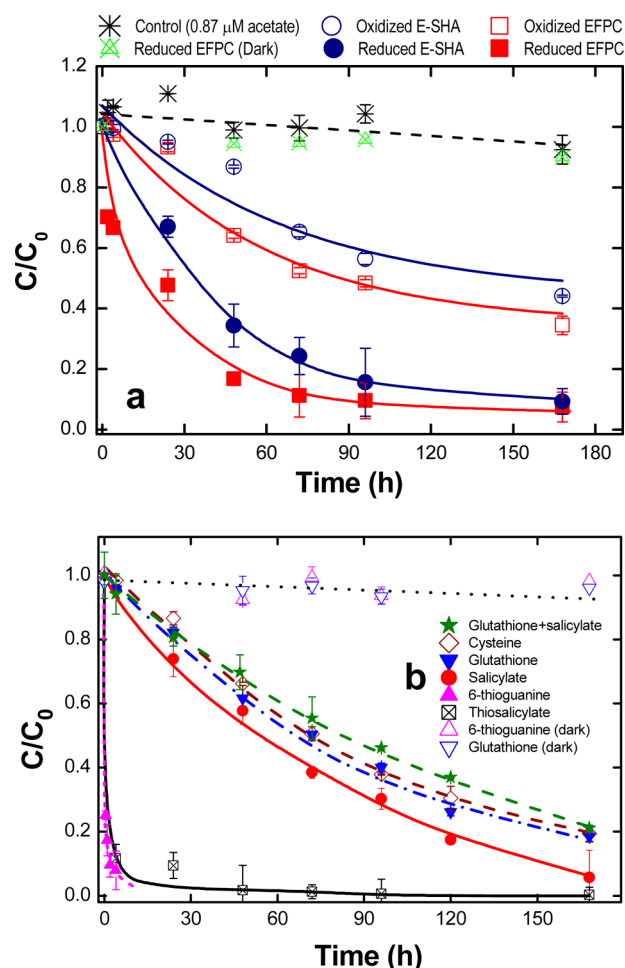
Figure 1. (a) Photodegradation of MeHg, expressed as the ratio of MeHg concentration at a given time (C) to that at time zero (C_0), as influenced by the presence of DOM under simulated solar irradiation. The reduced DOM was obtained by Pd/H$_2$ reduction,[20] and the final DOM concentration was 0.13 mM DOC. (b) Influences of organic ligands (cysteine, glutathione, salicylate, thiosalicylate, or 6-thioguanine, 2 μM each) or a mixture of glutathione and salicylate (1 μM each) on MeHg photodegradation. For the sake of clarity, representative controls are plotted; additional dark controls in the presence of DOM and organic ligands are plotted in Figure S5 of the Supporting Information. The initial added MeHg concentration (C_0) was 50 pM. All samples were prepared in a low-ionic strength simulated freshwater containing ∼1 mM KCl and 0.87 μM acetate with a final pH of 6.9 ± 0.1. Data points represent an average of duplicate or triplicate measurements from sacrificial sample vials, and error bars represent one standard deviation.

than that of salicylate at the same ligand concentration (2 μM). A relatively high k_{d-ph} value [(3.6 ± 0.4) × 10^{-3} m^2 E^{-1}] was observed even in the presence of only 5 nM thiosalicylate (Table S1 of the Supporting Information). However, the thiol group alone in glutathione and cysteine (nonaromatics) did not result in a degradation rate as high as that of thiosalicylate, but the rate was similar to that of salicylate (Figure 1b). These results indicate that thiols in nonaromatic compounds are not as effective as previously thought in enhancing MeHg photodegradation.[17] Most notably, we found that a combination of a nonaromatic thiol with an aromatic compound (salicylate and glutathione, 1 μM each) did not result in an increased degradation rate either (Table S1 of the Supporting Information), suggesting that thiols and aromatic functional

groups on a single molecule (e.g., thiosalicylate and 6-thioguanine) worked synergistically in enhancing MeHg photodegradation.

As a soft Lewis base, thiolate forms a strong bond with Hg(II) and MeHg.[18,28−31] Formation of a complex between MeHg and S$^-$ weakens the C−Hg bond, causing a shift in H$_3$C−Hg$^+$ bond energies.[32,33] Theoretical studies and quantum mechanical calculations support the argument that coordination of thiols with MeHg drives the charge redistribution or increased negative charge on the C atom[32,33] and thus decreased electron transition energies of the C−Hg bond leading to its breakdown.[34] Reduction of DOM by H$_2$/Pd not only affects hydrogenation of DOM and the quantum yield of reactive species such as ^{3}DOM* but also converts the oxidized functional groups such as disulfide and sulfonate to thiolates or thiols in DOM.[20,35,36] This partially explains why MeHg photodegradation was 3-fold faster with reduced DOM than with oxidized DOM (Figure 1a and Table S1 of the Supporting Information).

These observations can be further elaborated by an increased rate of photodegradation of MeHg with increasing levels of thiols or thiol−MeHg complexes (Figure 2). The k_{d-ph} values were 0.8 × 10^{-3}, 1.8 × 10^{-3}, and 3.6 × 10^{-3} m^2 E^{-1} with increasing thiosalicylate concentrations of 0.1, 1, and 5 nM,
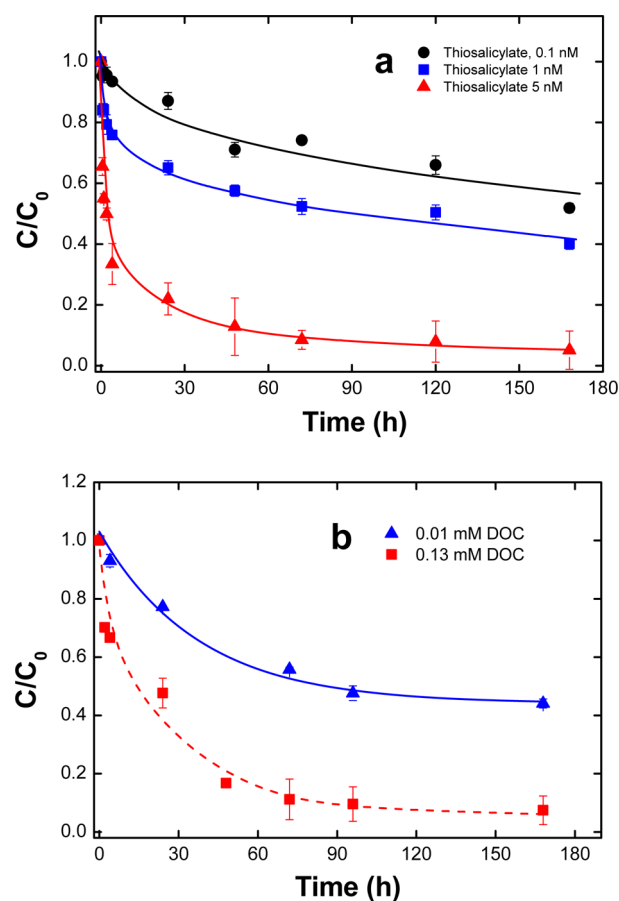

Figure 2. Influence of organic ligand concentrations on MeHg photodegradation under simulated solar irradiation: (a) thiosalicylate and (b) reduced EFPC-DOM. The initial MeHg concentration (C_0) was 50 pM. Experimental conditions and error bars are the same as described in the legend of Figure 1. No appreciable MeHg degradation occurred in the dark in the presence of DOM and organic ligands (see Figure S5 of the Supporting Information).

respectively, equivalent to thiol:MeHg molar ratios of 2:1, 20:1, and 100:1, respectively (Figure 2a and Table S1 of the Supporting Information). Using equilibrium chemical speciation calculations at the thiol:MeHg molar ratios given above (Table S2 of the Supporting Information), we found that ~40.1, 89.3, and 97.7% of the MeHg formed complexes with thiolate functional groups. At 2 μM, MeHg is completely complexed with the $-S^-$ in thiosalicylate. Similarly, increasing concentrations of reduced EFPC-DOM from 0.01 to 0.13 mM DOC increased k_{d-ph} from $(2.0 \pm 0.1) \times 10^{-3}$ to $(4.3 \pm 0.3) \times 10^{-3}$ m^2 E^{-1} (Figure 2b). Approximately 95% of MeHg was degraded after 1 week at 0.13 mM DOC, which is equivalent to a thiol:MeHg ratio of ~250 based on a reactive $-SH$ content of 4 nM/mg of DOM (or ~100 nM/mM DOC).[19,25,31] However, only ~60% of MeHg was degraded in the presence of 0.01 mM DOC (thiol:MeHg ratio of 20), again indicating that an increasing level of thiols led to an increased rate of MeHg photodegradation.

Consistent with studies by Black et al.[5] and Tai et al.,[16] we found that neither $^1O_2$ nor $^{\bullet}$OH radicals were important in MeHg photodegradation because the reaction rates were unchanged upon addition of radical inhibitors (NaN$_3$ for $^1O_2$ or isopropyl alcohol for $^{\bullet}$OH) to either EFPC-DOM or thiosalicylate (Figure 3a,b). On the other hand, addition of isoprene, a triplet state quencher, to reduced EFPC-DOM and salicylate decreased the photodegradation rates by ~50 and 80%, respectively (Figure 3c), suggesting that the triplet states of photosensitized ligands were responsible. The ^{3}DOM* triplet state has long been recognized in the photodegradation of various organic contaminants,[21,37,38] because aromatics and phenolic compounds in DOM are readily photosensitized because of their strong UV absorbing characteristics (Figure S1 of the Supporting Information).[21,22,37,38]

Previous studies also showed that, upon UV irradiation, salicylate and thiosalicylate can form excited triplet states, or carboxylphenyl radicals, in the presence or absence of oxygen.[39,40] Tossell[34] found that the creation of the lowest-energy triplets from MeHg compounds (CH$_3$HgL) is essential for MeHg photodegradation, in which CH$_3$HgL is decomposed into $^{\bullet}$CH$_3$ and $^{\bullet}$HgL radicals. However, this process is relatively slow in the absence of photosensitizing agents[34] but could be accelerated in the presence of DOM because the energy of the excited triplet state can be transferred to the C atom of the C−Hg bond in MeHg, leading to its cleavage. Strong binding between MeHg and $-S^-$ facilitates the direct energy transfer from the triplet state and thus increases the rate of C−Hg bond breaking. This explains why salicylate (nonthiol), cysteine or glutathione (nonaromatic) alone, or a combination of salicylate and glutathione is not as effective as thiosalicylate or 6-thioguanine in enhancing the photodegradation of MeHg (Figure 1b).

Our study thus demonstrates that when simultaneously present in a molecule, thiols and aromatics can work together, resulting in a rate of MeHg photodegradation far greater than that with either of them acting alone. The results support the recently proposed mechanism of MeHg photodegradation via intramolecular electron transfer,[16] although we note that the previous study failed to identify the effect of ^{3}DOM* on MeHg photodegradation. A possible explanation is that the Everglades water, used by Tai et al.,[16] contained a very high level of DOC (1.5 mM) but a low level of MeHg (0.6 pM), typical in natural waters.[5,6,11,16,25] This translates to a thiol:MeHg molar ratio of ~2.5 × 10^5:1. Our speciation calculations (Table S2 of the
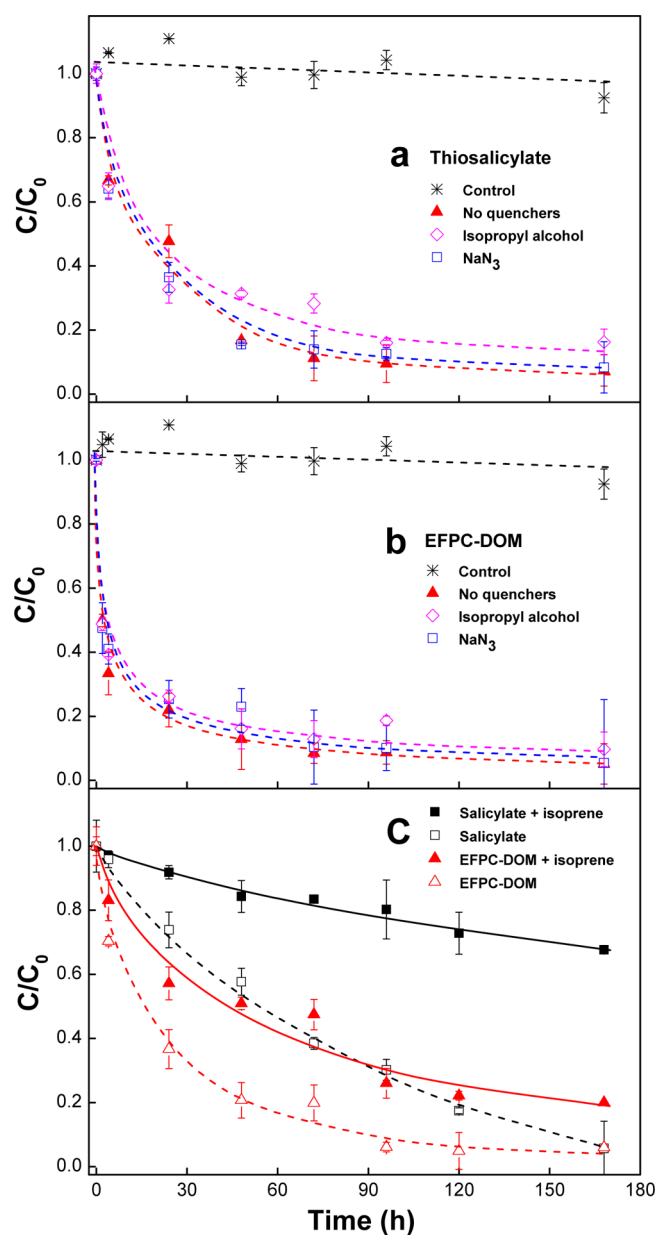

Figure 3. Effects of free radical inhibitors [i.e., NaN$_3$ at 10 mM or isopropyl alcohol at 0.01% (v/v)] on MeHg photodegradation in the presence of (a) reduced EFPC-DOM (0.13 mM DOC) and (b) thiosalicylate (5 nM) under simulated solar radiation. (c) Effects of isoprene (10 mM) on MeHg photodegradation in the presence or absence of salicylate (2 μM) and reduced EFPC-DOM. The initial MeHg concentration (C_0) was 50 pM. Other experimental conditions and error bars are the same as described in the legend of Figure 1.

Supporting Information) indicate that nearly 100% MeHg is already complexed with thiols at the thiol:MeHg ratio of ~10^2, so that a further increase in the thiol:MeHg ratio would be expected to show little influence in enhancing MeHg photodegradation, which is reflected in some studies that show a lack of DOM concentration-dependent effects on MeHg photodegradation.[5,6,12] On the other hand, this DOM-concentration dependent MeHg photodegradation can be expected in laboratory-prepared solutions containing a low thiol:MeHg ratio (0.006−50)[17] or through a series of dilutions of the Everglades water.[16] Furthermore, DOM is known to affect light attenuation, and thus, DOM aromaticity [measured

by specific UV absorptivity (SUVA) at 254 nm][41] may not correlate directly with the rate of MeHg photodegradation. Lower-molecular weight aromatics or phenolic compounds such as salicylate (Figure 3c) may also show photosensitization effects stronger than those of the conjugated aromatic compounds.[41,42] In our case, EFPC-DOM appeared to be slightly more effective than E-SHA in enhancing the degradation of MeHg, although E-SHA showed a SUVA value $[8.75 \text{ L (mg of C)}^{-1} \text{ m}^{-1}]$ higher than that of EFPC-DOM $[4.42 \text{ L (mg of C)}^{-1} \text{ m}^{-1}]$, regardless of whether they were reduced or oxidized.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Rate constants, chemical structure and UV absorbance spectra, spectrum of the simulated solar light, UV intensity and MeHg photodegradation under natural sunlight, and additional dark controls. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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