

Article

Effect of Benzophenone Type UV Filters on Photodegradation of Co-existing Sulfamethoxazole in Water

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Abstract: Benzophenones (BPs) frequently occur in water environments, and they are able to both screen UV light and to sensitize reactive intermediate (RI) production. However, BPs have largely been overlooked as a background water component when studying photodegradation of co-existing organic micropollutants (OMPs). Therefore, in this study, we investigated the influence of BP and its derivative oxybenzone (BP3) on the degradation of the co-existing model OMP sulfamethoxazole (SMX). A series of photodegradation experiments were conducted covering a range of BPs concentrations in $\mu\text{g/L}$ levels, and the degradation of 1.00 μM of SMX was studied. The addition of BP at 0.10 μM , 0.25 μM , and 0.30 μM , and BP3 at 0.10 μM and 0.25 μM , significantly increased the first order degradation rate constant of 1.00 μM of SMX ($k_{\text{obs(BP)}}$) by 36.2%, 50.0%, 7.3%, 31.5%, and 36.2% respectively, compared to that in the absence of any BPs. The maximum indirect photodegradation induced by BP and BP3 reached 33.8% and 27.7%, respectively, as a percentage of the observed SMX degradation rate at the [BPs]/[SMX] ratio of 0.25. In general, triplet excited dissolved organic matter ($^3\text{SMX}^*$, $^3\text{BP}^*$, and $^3\text{BP3}^*$) played the major role in the photosensitizing ability of BPs. The results further implied that the increase of SMX degradation at the molar ratio of 0.25 was possibly due to $^3\text{BP}^*$ for the mixture of SMX and BP. Overall, this study revealed the sensitizing ability of BP and BP3 on the co-existing OMP, SMX, in water for the first time. Our findings can be applied to other BP type UV filters which are similar to BP and PB3 in molecular structure.



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1. Introduction

Organic micropollutants (OMPs) are being increasingly detected in the environment, raising public as well as scientific concern [1]. They undergo physical (e.g., sorption, dilution), biological (e.g., biodegradation), and chemical (e.g., hydrolysis, photolysis) transformations in the environmental water [2,3]. Some OMPs are degraded through either biodegradation or photodegradation, while some degrade through both and some by neither [3]. For many OMPs, the photodegradation rate under sunlit conditions is known to be larger than their biodegradation rate [3]. In environmental water, OMP photodegradation rate is influenced by co-existing components either positively due to the generation of reactive intermediates (RIs) that promote indirect photolysis or negatively due to scavenging of RIs and the attenuation of light [4]. For instance, NO_3^- [5–11], Cl^- [10,11] and dissolved organic matter (DOM) [6–10] in the water column possibly contribute to generating RIs. In addition, some OMPs have also exhibited promoting effects on the photodegradation of other co-existing OMPs [12–14]. For instance, triplet excited aromatic ketones are able to react well with other aromatic compounds which contain electron-donating groups [15], such as phenolate ions [16] and phenols [17].

Among the OMPs detected in the water environment are UV filters/sunscreen products such as benzophenone derivatives, *p*-Aminobenzoic acid derivatives, camphor derivatives, benzotriazole derivatives, and salicylate derivatives [18]. Sunscreen products are

widely used for the protection of skin from carcinogenic effects that may result from the exposure to UV radiation. Among them, benzophenone (BP) derivatives are actively used components of organic sunscreens [16–19]. Besides, BP is used during the production of insecticides, agrochemicals, and pharmaceuticals as it serves as photo-initiator, UV curing agent, fragrance enhancer, and a flavoring agent. It is also used as an additive in plastics, coating products, and adhesives [19]. As a result of such extensive use, BP and its derivatives have been widely detected in surface water and wastewater treatment plants [20–24] among other organic micropollutants (OMPs).

Upon reception of photon energy in aqueous media, BP produces $^1\text{O}_2$, $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ through type I and II photodynamic reactions in a concentration dependent manner [25]. Furthermore, BP can abstract H from coexisting molecules through its excited triplet state [12]. In addition, fenofibrate, amiodarone [12], and fenofibric acid [13,14], which contain the carbonyl moiety as in BP and its derivatives, have shown photosensitization capabilities, sometimes exceeding the sensitizing effect of natural organic matter [13,14]. For instance, fenofibric acid, a chlorobenzophenone, accelerates the photodegradation process of the gemfibrozil fibrate drug under UV radiation via fenofibric acid's triplet excited state and $^1\text{O}_2$ [13]. Fenofibric acid also increases the degradation rate of coexisting bezafibrate via (1) triplet excited fenofibric acid and $^1\text{O}_2$, (2) the energy transfer of singlet excited fenofibric acid or degradation byproducts with dissolved oxygen, (3) e_{aq}^- , and (4) $\text{O}_2^{\bullet-}$ to a smaller extent, under solar irradiation [14].

However, despite their occurrence in environmental waters in a range of concentrations, the influence of BP itself and its sun-screening derivatives such as oxybenzone (BP3) has been largely overlooked as possible photosensitizers. For instance, BP has been acknowledged as one of the aromatic ketones, whose excited triplet state can oxidize other compounds such as phenylurea herbicides [15], phenols [17,26], phenolate ions [16], methoxybenzenes [27], amino acids and aminopolycarboxylic acids [28], and amines [29,30]. However, those studies have particularly focused on only BP's triplet excited state often through laser flash photolysis and have not investigated its influence in wide ranges of their concentrations. To be specific, considering BP's simultaneous ability to screen UV irradiation and sensitize RI production, their concentration dependent influence on the photodegradation of co-existing OMPs is yet to be understood in environmentally relevant concentrations. BPs typically have been detected in the environmental waters in ng/L to $\mu\text{g/L}$ levels [31–40]. For instance, BP and BP3 have been detected in surface water up to 82 ng/L [40,41] and 44,000 ng/L [31–43], respectively. Nevertheless, studies focusing on the sensitizing ability of BP or BP-like OMPs have employed degradation-target pollutants in mg/L level (i.e., 1–10 mg/L [13,14] and sensitizing OMPs also in mg/L level (i.e., 0.5–20.0 mg/L [13,14,25]). Considering that RI production by BP is concentration dependent [25], research covering a wide range of concentrations in ng/L or $\mu\text{g/L}$ is required to understand the sensitizing effect of BPs on co-existing OMPs in the environmental water.

Therefore, the objective of this research was to investigate the promotional/inhibitory influence of BP and its derivative BP3 on the degradation of co-existing OMPs at a range of concentrations in $\mu\text{g/L}$ level. It should be noted that this study did not include elucidating the reaction pathway of SMX degradation in the presence of BPs. To this end, we selected sulfamethoxazole (SMX) as a model target micropollutant and investigated processes responsible for the influence of BP and BP3 on photodegradation of SMX in a range of BP and BP3 concentrations. The selection of SMX as the model OMP was based on its frequent detection in surface water worldwide [44–49], its high dependence on photodegradation compared to other processes such as biodegradation [3], and its capability to undergo indirect photodegradation via $\bullet\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ [50–52]. Series of photodegradation experiments under simulated sunlight were conducted in combination with RI quenching experiments to understand dominant physical and chemical processes for the co-exposure degradation of SMX with BPs.

2. Materials and Methods

2.1. Material

SMX ($\geq 98\%$), BP (analytical grade), BP3 ($\geq 98\%$), methanol (MeOH) ($\geq 99.9\%$, high-performance liquid chromatography (HPLC) grade), sorbic alcohol (SA) (97%) were purchased from Sigma-Aldrich (Tokyo, Japan). HPLC grade acetonitrile (ACN) ($\geq 99.9\%$), *p*-nitroanisole (PNA, 97%), 2-propanol (IPA, $\geq 99.7\%$ for gas chromatography (GC)), pyridine (PYR, $\geq 99.5\%$ for GC), acetic acid ($\geq 99.7\%$) and superoxide dismutase (SOD, 5550 U/mg) were purchased from Kanto Chemicals (Tokyo, Japan). Phosphate buffer powder (1/15 mol/L, pH 7.0) and NaN_3 (99%) were purchased from Fujifilm Wako Pure Chemical corporation (Osaka, Japan) and Arcos Organics (Japan) respectively.

2.2. Chemical Actinometry Experiment

Photodegradation experiments were conducted using a photoreactor (HELIOS.Xe, Koike Precision Instruments, Hyogo, Japan), which is equipped with a 300 W Xe short arc lamp (Ushio, Tokyo, Japan), an optical filter between the lamp and samples to cutoff wavelengths less than 280 nm, and a temperature regulator which maintained the experimental system at 20 °C. In this reactor 10 quartz tubes placed around the lamp were irradiated simultaneously. The distance between the lamp and the inner-most surface of each quartz tube was 6 cm.

To determine photon irradiance ($E_{p,tot}^0$) and spectral photon irradiance ($E_{p,\lambda}^0$) for the wavelength range 280–400 nm at each tube position of the photoreactor, the chemical actinometry experiment was carried out using the chemical actinometer system containing PNA and PYR at initial concentrations of 10.00 μM ($[\text{PNA}]_0$) and 10.00 mM ($[\text{PYR}]_0$), respectively [53]. In this experiment PYR was added to accelerate the photoreaction of PNA. This experiment was conducted in triplicate with 10 mL of the actinometer in quartz tubes. After initiating radiation, samples were collected at 10-min intervals, up to 50 min, and the PNA concentrations were determined using an HPLC system (Prominence UFLC, Shimadzu, Kyoto, Japan) equipped with a UV-Vis absorbance detector (SPD-20 UFLC, Shimadzu, Kyoto, Japan) and a C18 column (Kinetex, Phenomenex Co., Torrance, CA, USA; 5 μm , 4.6 \times 250 mm) using a mobile phase of 60/40 MeOH/Milli-Q(MQ) (*v/v* %). After the measurement, the initial degradation rate constant of PNA for each tube position was determined and applied for calculating the irradiance at each of specific locations of the quartz tubes using the equations in Table S1.

2.3. Photodegradation Experiments

Photodegradation experiments were carried out at 20 °C using 10.00 mL solutions of SMX alone (1.00 μM) and with BP or BP3 (hereafter BPs) mixtures in phosphate buffer at pH 7 using the above-mentioned photoreactor. Samples were continuously stirred during the 10 h of each experiment. The molar ratio $[\text{BP or BP3}]/[\text{SMX}]$ was varied in the range 0.00–1.00 by fixing $[\text{SMX}]$ at 1.00 μM to investigate the influence of the proportion of BPs on SMX degradation. In addition, quenching experiments of RIs were conducted for SMX/BPs mixtures in the presence of IPA (2000 μM), NaN_3 (500 μM) SA (2500 μM) and SOD (3000 U/L) for quenching $\bullet\text{OH}$, $^1\text{O}_2$, $^3\text{DOM}^*$ (i.e., $^3\text{SMX}^*$, $^3\text{BP}^*$, and $^3\text{BP3}^*$ in this study) and $\text{O}_2^{\bullet-}$ respectively.

Samples of 0.6 mL were collected at 1, 2, 4, 6, 8, and 10 h during photodegradation experiments with and without quenchers. SMX concentration in the collected samples were determined using an HPLC system (Prominence UFLC, Shimadzu, Kyoto, Japan) equipped with a UV-Vis absorbance detector (SPD-20 UFLC, Shimadzu, Kyoto, Japan) and a C18 column (Kinetex, Phenomenex Co., Torrance, CA, USA; 5 μm , 4.6 \times 250 mm). A 50/50 ACN/MQ (*v/v* %) mobile phase containing 0.1% acetic acid was used for determining SMX concentration. The flow rate and column temperature were set at 0.60 mL/min and 40 °C, respectively. The average relative error in the HPLC measurement was 4%.

2.4. Data Analysis

The experimental results were analyzed to quantify the inner filter effect and the sensitizing effect of BPs on the photodegradation of SMX. Wavelength dependent light screening factor caused by BPs (s_λ) is given by Equation (1) [54,55] where α_λ is the light attenuation coefficient of BP (/cm), ϵ'_λ is the molar absorption coefficient of SMX (L/cm. mol), l is the light path length (cm) calculated according to Equation (2) using the internal radius of the cylindrical quartz tube r ($r = 0.8$ cm) and $[\text{SMX}_0]$ is the initial SMX concentration (1.00×10^{-6} M). Equation (1) can be modified into Equation (3) by substituting α_λ with $2.303 \epsilon_\lambda [\text{BP}_0]$ where ϵ_λ is the molar absorption coefficients of BPs (L/cm. mol) and $[\text{BP}_0]$ is the initial BPs concentration (0.10×10^{-6} M– 1.00×10^{-6} M) [56]. Then, s_λ and the total light screening coefficient (S) induced by each concentration of BPs were calculated using Equations (3) and (4), respectively [54–56].

$$s_\lambda = \frac{1 - (10^{-(\alpha_\lambda + \epsilon'_\lambda [\text{SMX}_0])l})}{2.303 (\alpha_\lambda + \epsilon'_\lambda [\text{SMX}_0])l} \quad (1)$$

$$l = \frac{\pi r^2}{2r} \quad (2)$$

$$s_\lambda = \frac{1 - (10^{-(2.303 \epsilon_\lambda [\text{BP}_0] + \epsilon'_\lambda [\text{SMX}_0])l})}{2.303 (2.303 \epsilon_\lambda [\text{BP}_0] + \epsilon'_\lambda [\text{SMX}_0])l} \quad (3)$$

$$S = \frac{\sum I_\lambda s_\lambda \epsilon'_\lambda}{\sum I_\lambda \epsilon'_\lambda} \quad (4)$$

where I_λ is the lamp irradiance at a specific wavelength λ (280–400 nm).

Since the absorbance of tested OMP mixtures was minor in the visible light region (400–800 nm), it was excluded from the analysis. UV-visible absorption spectra of BPs and SMX individually at each concentration used for experiments were obtained using a UV-vis spectrophotometer (UV1800, Shimadzu, Kyoto, Japan). Subsequently, the obtained absorbance spectra were used in calculating ϵ'_λ using the Beer-Lambert law (Equation (5)),

$$A_\lambda = \epsilon'_\lambda L [\text{SMX}_0] \quad (5)$$

where A_λ is the measured absorbance at a given wavelength λ and L is the optical path length (1 cm). Then, the calculated S value was used to obtain the direct and self-sensitized photolysis rate constant of SMX (k_{d+s} , Equation (6)) and indirect photolysis rate constant initiated by BPs (k_{ind}) was estimated using Equation (7).

$$k_{d+s} = S k_{obs(non\ BPs)} \quad (6)$$

$$k_{obs(BPs)} = k_{d+s} + k_{ind} \quad (7)$$

where $k_{obs(non\ BPs)}$ is the observed photolysis rate constants of SMX in the absence of BP (h^{-1}) and $k_{obs(BPs)}$ is the observed photolysis rate constants of SMX in the presence of BP (h^{-1}). In the presence of BPs, $k_{obs(non\ BPs)}$ is reduced to k_{d+s} by the inner filter effect/light screening of BPs and this reduction is accounted for by S (Equations (3) and (6)). Hence, the enhanced SMX degradation owing to the sensitization by BPs was estimated by k_{ind} in Equation (7).

3. Results and Discussion

3.1. Effect of BP and BP3 on the Photodegradation of SMX

In the absence and presence of BPs, SMX degradation followed 1st order photodegradation kinetics with $R^2 \geq 0.97$. Figure 1 shows the photodegradation kinetics for some selected $[\text{BPs}]/[\text{SMX}]$ molar ratios 0.00–0.30.

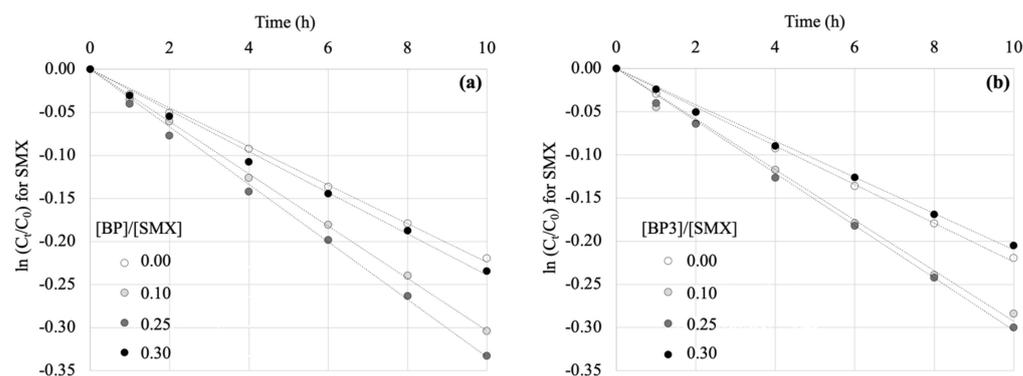


Figure 1. First order photodegradation kinetics for SMX in the absence and presence of (a) BP and (b) BP3 (for selected [BPs]/[SMX] ratios). Experimental conditions: [SMX]₀ = 1.00 μM, pH = 7.0, temperature = 20 °C, degradation time = 10 h.

Consequently, the first order degradation rate constant of SMX was influenced by the coexisting BPs depending on the molar ratio (Figure 2) (hereafter [BP]/[SMX] and [BP3]/[SMX] will be referred to as BP ratio and BP3 ratio respectively) (Figure 2a). At BP ratios of 0.10 and 0.25, an obvious promotion of the SMX degradation by BP was evident. For BP ratios of 0.10 and 0.25, $k_{obs(BP)}$ increased by 36.2% and 50.0%, respectively, relative to the negative control (i.e., in the absence of BP) (Figure 2b). At the BP ratio 0.25, the degradation rate of SMX was the maximum at $3.34 \times 10^{-2} \text{ h}^{-1}$ for the tested range of [BP]/[SMX].

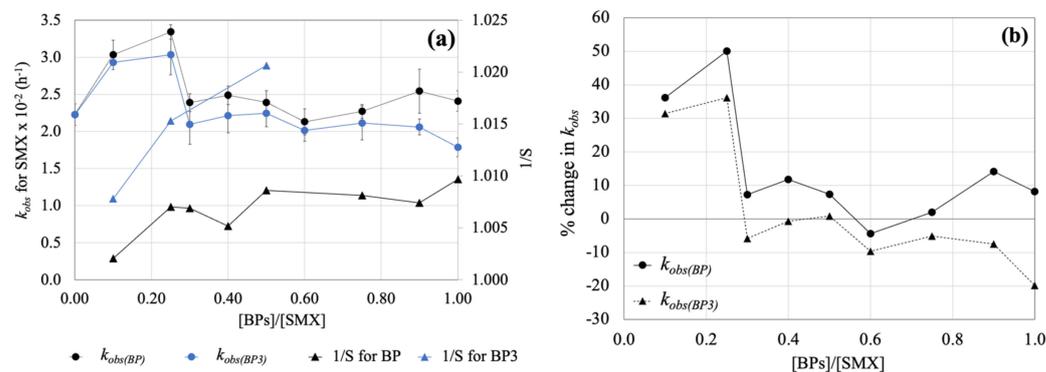


Figure 2. The relation between [BPs]/[SMX] and observed rate constant (k_{obs}). (a) k_{obs} for SMX (circles) and the inverse of total light screening coefficient (S) (triangles) at different molar ratios. The inverse of S corresponds to the light absorption. Error bars indicate a standard deviation of triplicated experiments. (b) Percentage change in $k_{obs(BPs)}$ for SMX compared to $k_{obs(non\ BPs)}$.

Similarly, for SMX irradiated with BP3, a significant increase in the first order degradation rate constant for SMX was observed for BP3 ratios of 0.10 and 0.25 (Figure 2b). The increase was 31.5% and 36.2% for the ratios of 0.10 and 0.25, respectively. The maximum SMX degradation rate was observed to be $3.03 \times 10^{-2} \text{ h}^{-1}$ at the BP3 ratio 0.25. All other BP3 ratios exhibited a decrease of the SMX degradation rate compared to the negative control except for the BP3 ratio 0.50 where the rate remained almost similar to that of SMX irradiated alone. The largest inhibition of SMX degradation was observed at the BP3 ratio of 1.00. Overall, at the lower ratios of 0.10 and 0.25, BP promoted SMX degradation slightly more than BP3 (Figure 2b).

At the BP ratios of 0.10, 0.25, and 0.30, k_{ind} accounted for 26.7%, 33.8%, and 7.4% of the corresponding $k_{obs(BP)}$ values, respectively (Figure 3, Table S2). At BP3 ratios of 0.10 and 0.25, k_{ind} accounted for 24.5% and 27.7% of the corresponding $k_{obs(BP3)}$ values, respectively. The contribution of BP to enhancing SMX degradation at the lower molar ratios (i.e., 0.10 and 0.25) was slightly higher than those of BP3 (Table S2). It should be noted

that the calculation was not carried out for BPs molar ratios that inhibited SMX degradation compared to $k_{obs (non BP)}$. Furthermore, k_{ind} as a percentage of $k_{obs (BPs)}$ in the presence of BP and BP3 increased as BPs ratios increased in the low range (i.e., 0.00–0.25) (Figure 3). This indicates that, within such low range, the sensitizing effect of BP dominantly determined the overall degradation rate of SMX, making the inner filter effect minor. Beyond the BP ratio of 0.25, k_{ind} as a percentage of $k_{obs (BP)}$ remained more or less stable approximately around 7.5%, indicating that the sensitizing effect no longer significantly increased with the increase of BP. As for BP3, the ratio of 0.25 showed the maximum $k_{ob (BP3)}$ value and all other ratios beyond 0.25 inhibited the SMX degradation. As BP3 shows a higher absorbance than BP in the wavelength range of 280–400 nm (Figure S1), it likely showed a more significant inner filter effect on SMX than BP.

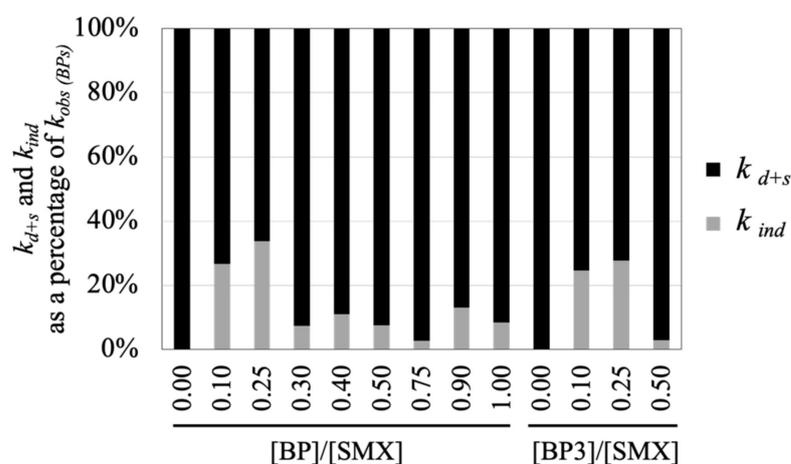


Figure 3. k_{d+s} and k_{ind} as a percentage of $k_{obs (BPs)}$ for BP and BP3 molar ratios, indicating the enhanced SMX degradation.

In a relevant study, k_{ind} initiated by 20 mg/L of fulvic acid in the Suwannee River accounted for 11% of k_{obs} of 3.65 μM of 2-phenylbenzimidazole-5-sulfonic acid (between 290–350 nm) [54]. Another study reported that k_{ind} initiated by 5 mg-C/L of fulvic acid and humic acid in the Suwannee River, Pony Lake fulvic acid, and Nordic aquatic fulvic acid, respectively, accounted for 33.0%, 38.6%, 35.7%, and 45.4% of the k_{obs} value of 2,3-dibromopropyl-2,4,6-tribromophenylether (between 290–320 nm) [55]. These experimental results indicate that BP and BP3 can be of similar significance as natural organic matter which are considered an important source of photosensitization for photodegrading co-existing OMPs in the water environment.

Overall, the shift of the SMX photodegradation rate in the presence of BPs was owing to the inner filter effect and the sensitizing effect caused by the BPs. According to the UV visible spectra, the BPs showed higher absorbance than SMX within the wavelength range 280–400 nm (Figure S1). Thus, light screening by BPs significantly affected the degradation rate constant of SMX when the concentration of BPs was relatively high (Figure 2b). According to the UV-visible spectra of BP and BP3 (Figure S1), BP3 has a larger absorbance than BP. This must have resulted in the inhibition of SMX degradation at higher BP3 ratios, in comparison to BP (Figure 2a).

Furthermore, fenofibric acid, which is a pharmaceutical containing the BP moiety, has also been reported to accelerate the degradation of 20.0 μM of gemfibrozil [13] and 13.8 μM of bezafibrate [14]. The acceleration of the degradation of those OMPs by fenofibric acid was in the order of 3.14 μM > 1.57 μM > 0.31 μM of fenofibric acid. This means that the sensitization ability continues to increase when the molar ratios [fenofibric acid]/[gemfibrozil] increases from 0.02 to 0.16 and [fenofibric acid]/[bezafibrate] increases from 0.02 to 0.23. These enhanced effects are identical to our experimental results for BPs and interestingly the molar ratios of OMPs are similar between the present and those studies. At the same time, the concentration of SMX (1.00 μM) in our study was much lower than those in the

reported investigations [13,14]. Nevertheless, in the current study, BPs exhibited the ability to screen light, which caused inhibition of SMX degradation at most of the higher BPs molar ratios alongside acting as a sensitizer. Thus, among the limited studies focusing on co-exposure photodegradation of OMPs, our study added new evidence enhancing our understanding on their interactive reactions under sunlit environment.

3.2. Effect of RIs in SMX Photodegradation with BP and BP3

In the absence of any BPs, quenchers SA, SOD, NaN₃, and IPA reduced the degradation coefficient of SMX (k_{d+s}) by 45.0%, 15.6%, 9.3%, and 6.4%, respectively. Thus, the contribution of RIs for SMX photodegradation followed the order ${}^3\text{SMX}^* > \text{O}_2^{\bullet-} > {}^1\text{O}_2 > \bullet\text{OH}$ (Figure 4). This result agreed with the observation by Zhou et al., (2015) [51], where ${}^3\text{SMX}^*$ exhibited the most contribution to SMX degradation and ${}^1\text{O}_2$ and $\bullet\text{OH}$ showed smaller contributions at pH 8, when SMX (the initial concentration, 3.95 μM) was irradiated in UV-visible light including UV-C. According to Zhou et al., (2015) and Lin et al., (2023) [52], SMX is capable of undergoing self-sensitized indirect photodegradation through ${}^1\text{O}_2$, $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$ produced in the presence of O_2 and H_2O via ${}^3\text{SMX}^*$. In addition, SMX undergoes direct photolysis through ${}^3\text{SMX}^*$ when irradiated [51,52]. Considering that SA quenching caused the largest inhibition of SMX degradation rate, direct photolysis is the more prominent process for the degradation of irradiated SMX than its self-sensitized photodegradation, which was also supported by the largest reduction in $k_{obs (non BP)}$ in the SA quenching (Figure 4).

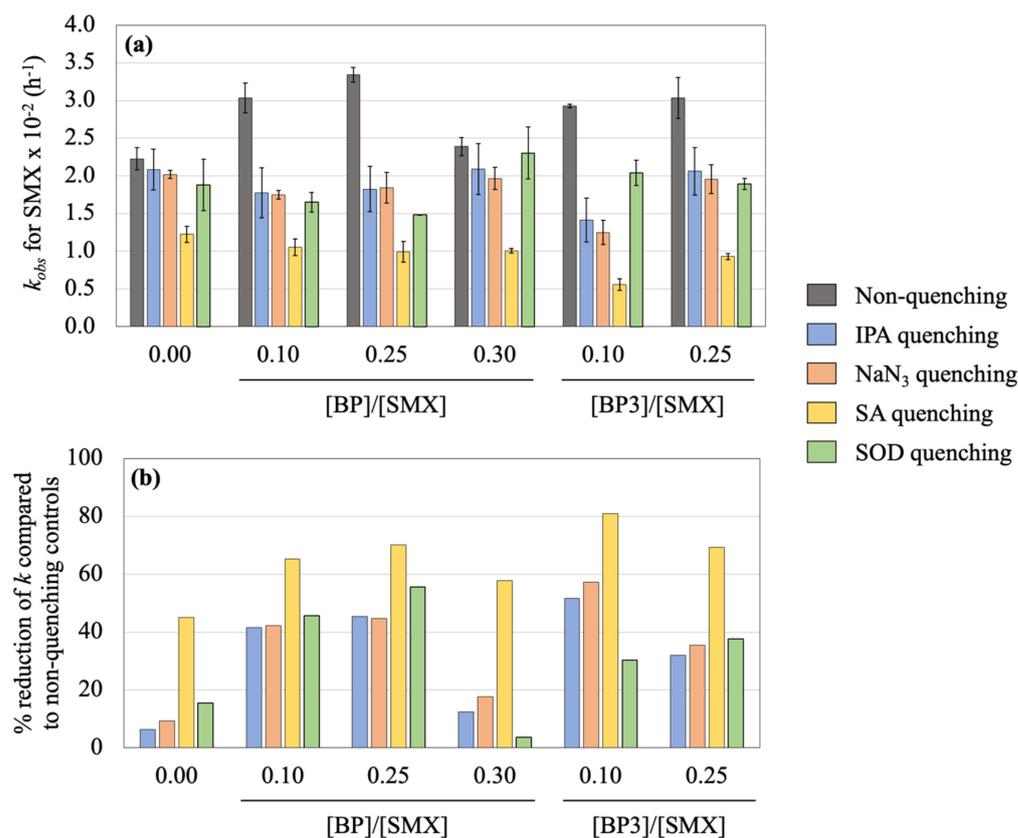


Figure 4. The change of k_{obs} in the quenching experiment. (a) First order degradation rate constant of SMX in the absence ($k_{obs(non BP_s)}$) and presence ($k_{obs(BP_s)}$) of BPs with and without quenchers and (b) the reduction of $k_{obs(non BP_s)}$ and $k_{obs(BP_s)}$ in the presence of quenchers, as a percentage of those in the absence of quenching.

In case of the presence of BPs, ${}^3\text{SMX}^*$, ${}^3\text{BP}^*$, and ${}^3\text{BP3}^*$ quenching by SA caused the largest reduction of degradation rate of SMX for all tested BP and BP3 ratios (Figures 4b and 5). Hence, triplet excited states are the most significant for the degradation of SMX in the

presence of BPs. The addition of BP at ratios 0.10 and 0.25 significantly contributed to SMX degradation via $\bullet\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ radicals as shown in IPA, NaN_3 , and SOD quenching, respectively. Compared to their respective non-quenching controls, each of $\bullet\text{OH}$, $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$ respectively contributed to 41.5%, 42.3%, and 45.6% of SMX degradation at the BP ratio of 0.10 and to 45.4%, 44.8%, and 55.7% at the BP ratio of 0.25. The largest reduction of k_{obs} was observed at the BP ratio 0.25 for all quenchers. In fact, BP produces $^3\text{BP}^*$ upon irradiation, and then $^3\text{BP}^*$ can produce $^1\text{O}_2$ by energy transfer to O_2 , abstract H from C-H bonds of alcohols, and produce $\bullet\text{OH}$ in the presence of H_2O [12,57]. Therefore, the experiment of quenching $^3\text{SMX}^*$ and $^3\text{BP}^*$ reasonably displayed the highest inhibition of SMX degradation. Furthermore, the percentage reduction of $k_{obs(BP)}$ (Figure 4b) has increased when BP ratio increased from 0.00 to 0.25. Hence, the increase of k_{ind} from the BP ratio 0.10 to BP ratio 0.25 (Figure 3) is likely attributed mainly to the production of $^3\text{BP}^*$.

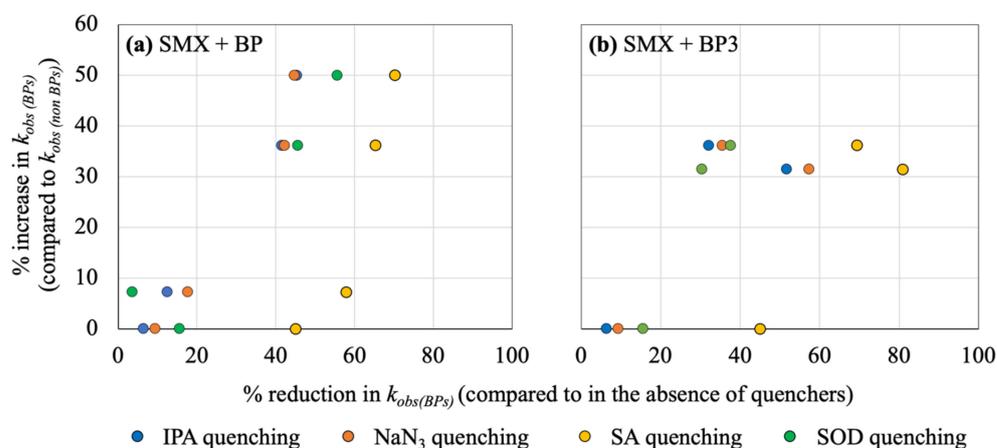


Figure 5. Relations between the percentage reduction in $k_{obs(BPs)}$ compared to in the absence of quenchers and the percentage increase in $k_{obs(BPs)}$ compared to $k_{obs(non BPs)}$ and for (a) BP ratios 0.00, 0.10, 0.25 and 0.30 and (b) BP3 ratios 0.00, 0.10 and 0.25.

Similar to BP, SA quenching experiments in the presence of BP3 in ratios 0.10 and 0.25 caused the largest inhibition of SMX degradation out of the four quenchers. This indicates that BP3 also promotes SMX degradation through pathways involving triplet excited states (Figures 4b and 5). Compared to the non-quenching controls, $\bullet\text{OH}$ quenching caused the reduction in SMX degradation rate by 51.7% and 32.1% at BP3 ratios 0.10 and 0.25, respectively. $^1\text{O}_2$ quenching at those ratios reduced the SMX degradation by 57.3% and 35.5% and $\text{O}_2^{\bullet-}$ quenching by 30.4% and 37.6%. At the same time, the highest contribution by $\bullet\text{OH}$, $^1\text{O}_2$ and $^3\text{SMX}^*/^3\text{BP3}^*$ was observed at BP3 ratio 0.10 while that for $\text{O}_2^{\bullet-}$ was highest at BP3 ratio 0.25. The contribution of each RI to SMX degradation decreased when the BP3 ratio was increased from 0.10 to 0.25 except for the $\text{O}_2^{\bullet-}$. The contribution of $\text{O}_2^{\bullet-}$ increased by about 7% when the BP3 ratio increased from 0.10 to 0.25. It should be also noted that the sum of the reductions of $k_{obs(BPs)}$ in the presence of quenchers for some BP or BP3 ratios exceeded 100%, possibly due to simultaneous quenching of non-targeted RIs [58]. Nevertheless, BP3 exhibited a better sensitizing ability for SMX degradation at the tested lower BP3 ratios.

In the degradation process of SMX, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ can attack the isoxazole ring, the benzene ring, or the S-N bond of SMX molecules to form several intermediate products [50,59]. Those reactions go through three main pathways, which are hydrogen abstraction, hydroxylation, and electron transfer. For $\bullet\text{OH}$ specifically, hydrogen abstraction and hydroxylation play an important role to initiate SMX degradation. The intermediates produced through reaction of $\bullet\text{OH}$ with SMX contain free radicals and thus they can undergo further reactions [50]. In addition, triplet aromatic carbonyls such as $^3\text{BP}^*$ are known to react with amines in aqueous media [30]. SMX contains an amine group and thus it is likely to react directly with the triplet states of BP and BP3. Hence, the direct

reactions of $^3\text{BP}^*$ and $^3\text{BP3}^*$ with SMX in addition to the production of RIs justify the overall sensitizing effect of BPs as well as those triplet states being the most important species for promoting SMX degradation.

Overall, the quenching experiments revealed that the most important RI for sensitizing SMX degradation by BP and BP3 is their triplet excited states. This result is reasonable as SMX produces $^1\text{O}_2$, $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$ in the presence of O_2 and H_2O via $^3\text{SMX}^*$ [51,52]. Furthermore, BP produces $^1\text{O}_2$ in the presence of O_2 and $\bullet\text{OH}$ [12,57] and $\bullet\text{OH}$ is an effective non-selective RI for the photodegradation of most OMPs [4,60]. As explained earlier in the discussion, these BPs have been proven to be as significant as natural organic matters in sensitizing indirect photodegradation of OMPs. Therefore, our study could be a steppingstone for acknowledging these commonly found BPs and other similar organic pollutants as important background constituents in assessing OMP degradation.

Our experiments were conducted under environmentally relevant $\mu\text{g/L}$ level concentrations of SMX and BPs at pH 7 and 20 °C. The outcome indicated that the influence of BPs on SMX degradation was a combination of the inner filter effect and sensitization of RIs initiated by BPs and SMX, which appeared to be concentration dependent. Both BP and BP3 sensitized SMX degradation significantly at concentrations 0.10 and 0.25 μM . In addition, SMX degradation was enhanced at all tested BP ratios except 0.60 and BP3 did not show any significant enhancement in SMX degradation at other tested ratios. The improvement of the photodegradation of SMX in these lower ranges of BPs ratios indicates that the sensitizing effect by BPs overpowers their light screening effect. In previous studies [13,14], the target OMP's concentration was always higher than the concentration of sensitizing OMPs, for instance 5.0 mg/L of gemfibrozil in the presence of 0.1, 0.5, and 1.0 mg/L of fenofibric acid, where gemfibrozil degradation has been promoted by fenofibric acid at all tested concentrations [13]. In our study, for the first time, inhibitory or promotional behavior of BPs was revealed by covering molar concentrations equal to and greater than the target OMP (i.e., SMX).

Overall, this experimental study demonstrated the ability of BP and BP3 to sensitize the production of RIs and thus promote degradation of co-existing OMPs in water. In the current study, the experiments were conducted in pH 7.0 buffer containing only the BPs and SMX, which is a relatively simple water matrix compared to environmental water. Our outcomes might not always be valid in the context of actual waters matrices. Thus, the concentration-dependent mechanism of BPs to sensitize RIs production is yet to be investigated to fully understand the competitive actions of RIs production and light screening, which influences the degradation of coexisting OMPs. To this end, for instance, complex water matrices including natural organic matter should be employed in further experimental study. Furthermore, the presented study did not elucidate the reaction pathway of SMX with the produced intermediates in the presence of BP or BP3. Therefore, the elucidation of the reaction pathway of SMX in the presence of BPs using mass spectrophotometry would be one of the next challenges in further study.

Nevertheless, major outcomes from this study are possibly applicable to other BP type UV filters (e.g., sulisobenzene (BP4) and dioxybenzone (BP8)) as they have similar molecular structures to BP and BP3. It would be worthwhile further exploring those similar compounds in the context of photodegradation of OMPs (i.e., SMX and others) considering their widespread use and frequent detection in water environments. In this regard, this study should be extended to other types of OMPs that are resistant to direct photodegradation in the natural environment in further investigation.

4. Conclusions

The overall objective of this study was to investigate the influence of co-existing benzophenone UV filters (BP and BP3) on photodegradation of SMX. The experiments using the photoreactor clearly showed that photodegradation of SMX was influenced by the co-existing BP and BP3 and this effect was concentration dependent. Both BP and BP3 enhanced SMX degradation in the low ranges of concentration including 0.10 and

0.25 μM . In addition, the quenching experiments further revealed that the photolysis of SMX is promoted by radicals $\bullet\text{OH}$, $^1\text{O}_2$, $\text{O}_2^{\bullet-}$ and $^3\text{SMX}^*/^3\text{BP}^*/^3\text{BP3}^*$, which also depends on the concentration of BPs. Among them, $^3\text{SMX}^*/^3\text{BP}^*$ played the dominant role in the sensitizing process of SMX/BP mixtures.

This is the first investigation showing the sensitizing ability of BP and BP3 in the context of coexisting OMP photodegradation, employing a wide range of concentrations in $\mu\text{g/L}$ levels. The outcomes of this study could be applied to other BP type UV filters considering their molecular similarity to the studied BPs. Further investigation is expected regarding the sensitizing behavior of the BPs in the presence of natural organic matters and other complex water matrices to gain sufficient understanding on the fate of OMPs in the water environment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/photochem3020017/s1>, Table S1: Equations and calculations used in chemical actinometry experiment; Table S2: Results of the data analysis of indirect photodegradation induced by the BPs in the experimental system; Figure S1: UV absorbance spectra from 280 nm to 400 nm for 1.00 μM of SMX, BP, and BP3 measured using UV-vis spectrophotometer (UV2600, Shimadzu, Kyoto, Japan).

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