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Ozonation and peroxone oxidation of benzophenone-3 in water: Effect of operational parameters and identification of intermediate products

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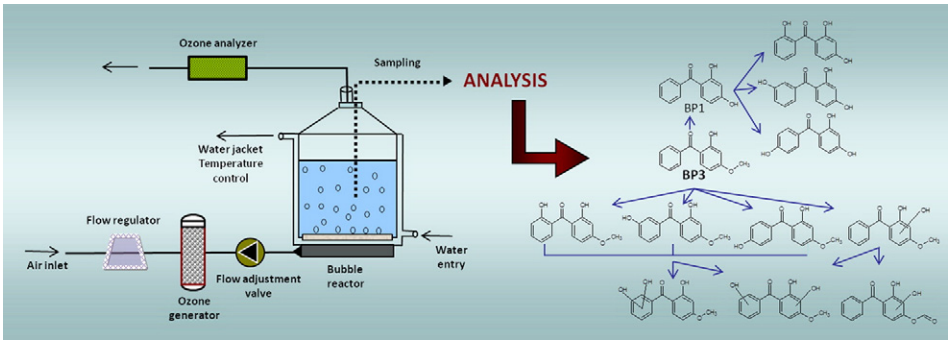
HIGHLIGHTS

- Ozonation shows to be a promising technology for the elimination of BP3.
- New data are obtained on the effect of process parameters on BP3 removal.
- Conditions favoring hydroxyl radical formation accelerate the degradation process.
- The reactivity is higher through radicalar pathways compared to direct ozonation.
- Seven major transformation products of BP3, including BP1 and DHMB, are identified.

GRAPHICAL ABSTRACT



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ABSTRACT

The goal of this study was to bring forward new data and insights with respect to the effect of operational variables and reaction pathways during ozonation and peroxone oxidation of the UV filter compound benzophenone-3 (BP3) in water. A systematic parameter study, investigating the effect of the ozone inlet concentration, temperature, pH, H_2O_2 and t-butanol addition in a lab-scale bubble reactor, showed the promising potential of ozonation towards BP3 degradation. pH showed to be a major process parameter, with half-life times (5.1–15.0 min) being more than two times shorter at pH 10 compared to neutral and acid conditions. This indicates the important role of hydroxyl radicals as supported by the addition of H_2O_2 and t-butanol as HO• promoter and scavenger, respectively. Ozonation intermediate products were identified by liquid chromatography coupled to quadrupole-time-of-flight mass spectrometry (HPLC–QqTOF-MS/MS). Demethylation and non-selective HO• attack proved to be the major reaction mechanisms. Where available, identified intermediates were confirmed using analytical standards, and concentration profiles along the ozonation process were determined through selective targeted MS/MS analysis. Benzophenone-1 (BP1), also being a UV-filter compound, and 2,2′-dihydroxy-4-methoxybenzophenone (DHMB) revealed to be the major BP3 degradation products, showing a maximum concentration at about the half-life time of BP3.

1. Introduction

Benzophenone-3((2-hydroxy-4-methoxyphenyl)-phenylmethadone, BP3) absorbs and dissipates UV irradiation, and constitutes one of the most commonly used UV filters. This compound is used in personal care products such as cosmetics, beauty creams, lotions and shampoos, or as

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an additive in polymeric materials that have to be protected from sunlight-initiated disruption (FDA, 1999; Council Directive, 1976).

Recent studies (Fent et al., 2010a; Gago-Ferrero et al., 2012a) indicate that sunscreen agents, including BP3, are persistent and bio-accumulative compounds (Log K_{OW} = 3.79, http://www.syrres.com/esc/physdemo.htm). The increasing use of UV filters constitutes a potential risk for the environment. BP3 was detected in several environmental matrices such as in surface waters (Balmer et al., 2005), sediments (Gago-Ferrero et al., 2011a) and fish (Fent et al., 2010a), as well as in human milk (Hany and Nagel, 1995; Schlumpf et al., 2010). BP3 shows estrogen-like activity in in vitro and in vivo assays (Schlumpf et al., 2004; Calafat et al., 2008, Blüthgen et al., 2012). Dermal and oral administration of BP3 to rats and mice has shown alterations in liver, kidney, and reproductive organs (Calafat et al., 2008). A recent study of Kunisue et al. (2012) indicates that exposure to elevated levels of benzophenone type UV filter compounds may be associated with estrogen-dependent diseases such as endometriosis.

Current wastewater treatment techniques are not effective in removing UV filters (Li et al., 2007; Negreira et al., 2009). These compounds are preferably retained in sewage sludge (Gago-Ferrero et al., 2011b; Negreira et al., 2011), which might be further used as a fertilizer. BP3 was measured at relatively high values (37 to 3810 ng L^{-1}) in raw wastewater and primary effluent (Snyder et al., 2006). The latter value is not far from the predicted no observed effect concentration (PNEC) for BP3 (6000 ng L^{-1}, chronic effects), as estimated in a recent tentative environmental risk assessment for fish and *Daphnia magna* (Fent et al., 2010b). In this context, there is an urgent need of new approaches for wastewater treatment for the removal of UV-absorbing compounds.

Advanced oxidation processes (AOPs), which generate hydroxyl radicals (HO•), are a promising tool for the removal of persistent organic pollutants (POPs) at an acceptable cost (0.05–0.20 euros per m^3 for ozonation) (Joss et al., 2008). There is abundant information about removal of pharmaceuticals and pesticides via innovative physical–chemical processes, but for personal care products the data available are limited. The feasibility of BP3 removal from sewage or treated gray water by ozone has been demonstrated in a few studies (Table 1), but a detailed insight in the mechanisms and the parameters affecting ozonation and peroxone oxidation processes are lacking so far. There are some studies reporting the conversion of BP3 into other benzophenone-type degradation products like BP1 during fungal biodegradation (Gago-Ferrero et al., 2012b) or human metabolism (Okereke et al., 1993, 1995; Kunisue et al., 2012), but its behavior during advanced oxidation processes is largely unknown. Moreover, apart from mechanistic considerations, also the data reported on removal efficiency are somewhat ambiguous. For example, whereas Rosal et al. (2010) did not detect any BP3 elimination by ozone, other studies report removal efficiencies above 80%. Hernández-Leal et al. (2011) recently studied BP3 degradation in Milli-Q water along with 17 other micropollutants and their results evidenced that BP3 was removed up to 94% (from 673 to 40 ng L^{-1}).

Given the lack of data and knowledge in this field, the aim of this research was to systematically investigate the removal of BP3 in water when treated with ozone and/or hydrogen peroxide (H_2O_2). The scope is twofold. First, the focus is put on the effect of operational variables on BP3 removal and on the ozone consumption. To the author's best knowledge, this study constitutes the first one investigating the effect of important process parameters like pH, H_2O_2 addition, temperature, and inlet ozone concentration on the ozonation of UV filters. Second, by use of advanced analytical techniques based on liquid chromatography coupled to quadrupole-time-of-flight tandem mass spectrometry (HPLC–QqTOF-MS/MS), BP3 main ozonation and peroxone byproducts are identified and structurally characterized to gain insight in the advanced oxidation pathway of BP3 in water.

2. Materials and methods

2.1. Standards and reagents

BP3 (CAS N. 131-57-7) and BP1 (CAS N. 131-56-6) were purchased from Sigma-Aldrich (Germany). 2,2′-dihydroxy-4-methoxybenzophenone (DHMB, CAS N. 131-53-3) and 2,3,4-trihydroxybenzophenone (THB, CAS N. 1143-72-2) were supplied by Dr. Ehrenstorfer (Germany). The isotopically labeled compound 2-hydroxy-4-methoxy-2′,3′,4′,5′,6′-d5 (BP3-d5), used as an internal standard, was obtained from CDN isotopes (Canada). The organic solvents (>99.8% purity) methanol, acetone, acetonitrile and HPLC grade water were provided by Biosolve (The Netherlands). H_2O_2 (35 wt.%), KH_2PO_4, K_2HPO_4 and $NaB_4O_7 \cdot 10(H_2O)$ were supplied by Acros Organics (Belgium). H_3PO_4 (≥85%, 15 M) was obtained from Merck (Belgium). Clean dry air ([H_2O]<3.0 ppm_v; [CO_2]<1.0 ppm_v; [C_xH_y]<0.5 ppm_v) was provided by L'Air Liquide (Belgium). Solid phase extraction (SPE) was carried out with Oasis HLB cartridges (60 mg sorbent, Waters, Spain).

2.2. Experimental setup

The ozonation experiments were performed in a temperature controlled bubble column with a height of 41.8 cm and an inner and outer diameter of 10.3 and 14.1 cm, respectively. Ozone was generated in dry air by a LAB2B ozone generator (Ozonia, Switzerland) and after flow adjustment dosed through a sintered glass plate at the bottom of the reactor. The reaction solution was prepared by adding BP3 powder (0.219 mmol L^{-1} (50.0 mg L^{-1})) to deionized water at controlled temperature conditions. After stirring this oversaturated solution for 24 h, the undissolved fraction was removed by filtration over a 0.45 μm filter, and the reactor was filled with 2.4 L of the BP3 saturated aqueous solution (dissolved concentration, 22.3 μmol L^{-1} (5.1 mg L^{-1}); RSD = 5%, n = 10). At the standard conditions, i.e. those applied during the initial experimental setup, the ozone inlet concentration was 85.7 μmol L_{gas}^{-1}, the gas flow rate 120 mL min^{-1}, and the reactor temperature 25 °C. The ozone mass transfer coefficient (k_La) in the bubble column was determined to be 5.5 h^{-1} (De Witte et al., 2010). The gas holdup and specific gas–liquid contact area are calculated (Tizaoui et al., 2009; Heynderickx et al., 2011) to be 0.014 (dimensionless) and 15 m^2m^{-3}, respectively. The water was buffered by a 10.12 mM phosphate buffer (pH 3 and pH 7) or a 2.5 mM borax buffer (pH 10). For the peroxone experiments, H_2O_2 was added in concentrations of 10–600 μM. Ozonated liquid samples were taken by a tap at 6 cm water height. Since the liquid phase in

Table 1
Overview of reported studies dealing with the ozonation of BP3 in sewage water.

Type of water	Scale	Mode	Time (min)	AOD[a] (mg L^{-1})	C_o[b] (ng L^{-1})	Removal (%)	Reference
STP effluent	Lab-scale	Semi-batch	15	16.3	123	NR[c]	Rosal et al. (2010)
Tertiary effluent	Pilot-scale	Continuous	24	7.3	6	>83	Snyder et al. (2006)
Tertiary effluent	Full-scale	Continuous	180	5–6	311	20	Li et al. (2007)
Aerobically treated gray water	Lab-scale	Batch	45	1.22	285	>94	Hernández-Leal et al. (2011)

[a] AOD: applied ozone dose.
[b] C_o: initial BP3 concentration.
[c] NR: not removed.

the bubble column reactor can be considered to be well mixed under the action of the bubbles (Heynderickx et al., 2011; Beltran, 2004), this sample is representative for the liquid phase in the whole reactor. Immediately after sampling, the samples were flushed with nitrogen for 2 min at 15 mL min^{-1} in order to remove residual ozone. Blank experiments, performed at the same conditions as applied during BP3 degradation but without addition of BP3, were carried out to obtain ozone consumption profiles also in the absence of BP3. In order to discard the effect of photodegradation during the experiments, preliminary experiments were carried out with 22.3 μmol L^{-1} BP3 but without ozone addition, showing no significant variations in the BP3 concentration.

2.3. Analytical methods

The ozone concentration in the gas flow was measured by an ozone analyzer through UV-light absorption at 254 nm. Aqueous BP3 concentrations were measured by HPLC attached to a photodiode array detector (Surveyor, Thermo Finnigan) without preconcentration. For details, see the Supplementary material. Aqueous hydrogen peroxide concentrations were determined by spectrophotometry based on 2,9-dimethyl-1,10-phenanthroline (DMP) and Cu(II) (Kosaka et al., 1998). pH measurements were done using a Jenway 3310 electrode.

Identification of BP3 degradation products formed during the ozonation process was performed by means of HPLC–QqTOF-MS/MS using a Waters Acquity UPLC™ system attached to a QqTOF-Micro™ (Waters/Micromass, UK). Chromatographic separation and detection conditions are given in the Supplementary material. Full-scan analyses were carried out on selected samples in both positive (PI) and negative (NI) electrospray (ESI) ionization modes. Further MS/MS analyses were carried out on identified molecular ions for their structural characterization. Exact masses were calculated and the elemental composition of the molecular ions and their fragments were determined using the MassLynx V4.1 software.

The ozonated water samples selected for byproduct identification by HPLC–QqTOF-MS/MS were preconcentrated by SPE using Oasis HLB cartidges. The applied SPE method was based on that of Rodil et al. (2008). Briefly, the cartridges were preconditioned sequentially with 2.5 mL of methanol and 2.5 mL of deionized water at pH 4.5. Twenty mL of the sample at pH 4.5 was loaded. After drying the cartridge under vacuum, elution was performed with twice 2.5 mL of methanol, followed by concentration to dryness under a gentle nitrogen stream. Finally, the extracts were reconstituted with 0.5 mL 25:75 (v/v) acetonitrile–water solution containing the internal standard BP3-d_5.

For the identified intermediates having commercially available analytical standards, selective target analysis was performed to determine their concentrations in non-concentrated aqueous samples collected as a function of ozonation time. For the most sensitive analysis, a liquid chromatography hybrid triple quadrupole-linear ion trap mass spectrometry (HPLC–QqLIT-MS/MS) method operating in the selected reaction monitoring (SRM) mode (Gago-Ferrero et al., 2012b) was used.

3. Results and discussion

3.1. BP3 degradation at standard conditions

At the standard conditions described in Section 2.2 and at pH 7, BP3 showed a half-life time ($t_{1/2}$) of 12.6 min (n = 5) and a 95% removal efficiency after 40–50 min, indicating a good BP3 degradability by ozonation. The BP3 degradation and ozone consumption profiles, with the latter representing the ozone inlet minus the ozone outlet concentration as a function of time, are shown in Fig. 1. Considering the data points up to 5% of the initial BP3 concentration, pseudo-first order reaction kinetics relative to the BP3 concentration were observed:

$$\ln\frac{[BP3]_t}{[BP3]_0} = -k_1 t \quad (1)$$

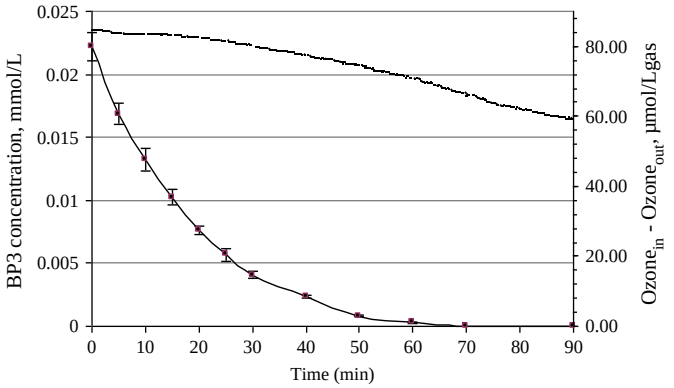

Fig. 1. Ozonation of BP3 at standard conditions (85.7 μmol L_{gas}^{-1} O_3, 25 °C, pH 7) (full line) and ozone consumption profile versus time (dotted line). Error bars represent standard deviations (n = 5).

in which $[BP3]_0$ and $[BP3]_t$ represent the BP3 concentration at time 0 and at reaction time t, respectively. The pseudo-first order rate constants ($k_{1,BP3}$) obtained at all investigated conditions are summarized in Table 2. These rate constants, which are function of the concentration of ozone, hydroxyl radicals and other oxidative species like $O_2^{\bullet-}$, $O_3^{\bullet-}$, $HO_2^{\bullet}$ and $HO_4^{\bullet}$, cannot be seen as fundamental reaction kinetics but they allow a quantitative comparison between the different experiments. At pH 7 and standard conditions, a $k_{1,BP3}$ value of 0.0556 min^{-1} (RSD = 6%, n = 5) was calculated. After 60 min of ozonation, 0.571 mmol (RSD = 5.4%, n = 5) of ozone was consumed, compared to 0.278 mmol for the blank experiment. The latter may be the result of ozone instability in aqueous systems. It may decompose and lead to complex radical mechanisms in which the hydroxyl radical is considered as the main responsible species for indirect reactions (Beltran, 2004).

3.2. Effect of the ozone inlet concentration

The effect of the inlet ozone gas concentration on the degradation of aqueous BP3 was investigated by dosing ozone at concentrations ranging from 32.6 to 151 μmol L_{gas}^{-1}, corresponding to an ozone load of 1.63 to 7.55 μmol min^{-1} L_{water}^{-1}. Other operational parameters, including the initial BP3 concentration, pH, and temperature were kept constant at 22.3 μmol L^{-1}, pH 7 and 25 °C, respectively. The experimental results (Table 2) revealed a faster BP3 removal at higher inlet ozone gas concentrations, with $k_{1,BP3}$ values increasing from 0.0229 to 0.1173 min^{-1}. This can be explained by an increased ozone concentration in the aqueous phase. Since BP3 is a non-volatile compound (vapor pressure = $7\cdot10^{-4}$ Pa at 25 °C), reactions in the gas phase are negligible. After the mass transfer of ozone from gas to liquid phase, however, it may either directly react with BP3 or decompose to produce other reactive species which in turn attack BP3. A linear relationship was found when the pseudo-first order constants $k_{1,BP3}$ were plotted against the gaseous ozone inlet concentrations ($y = 8.0\cdot10^{-4}x - 0.007$ ($R^2 = 0.992$, n = 5)), with the intercept not significantly different from zero ($\alpha > 0.05$).

The ozone consumption after 60 min of ozonation increased from 0.240 to 0.900 mmol. Plotting the ozone consumption versus the ozone inlet concentration also yielded a linear relationship ($y = 5.7\cdot10^{-3}x + 0.066$ ($R^2 = 0.994$, n = 5)), which means that, within the concentration interval studied, the ozone consumption is first order in the ozone inlet concentration. The total increase in ozone consumption might be explained not only by a faster BP3 degradation, but also by the formed reactive species and BP3 degradation byproducts.

3.3. Temperature effect

The effect of reaction temperature on the BP3 ozonation was investigated between 25 °C and 65 °C (Table 2). Within this range,

Table 2
Pseudo-first order BP3 rate constants and ozone consumption during 60 min of ozonation for experiments at 22.3 μmol L^{-1} initial BP3 concentration (RSD: relative standard deviation; n: number of repetitions).

Inlet O_3 concentration (μmol L_{gas}^{-1})[a]	Temperature (°C)	pH	H_2O_2 (μmol L^{-1})	t-butanol (mM)	$k_{1,BP3}$ (min^{-1}); RSD (%)	O_3 consumption during 60 min (mmol)
32.6	25	7	–	–	0.0229	0.240
61.2	25	7	–	–	0.0421	0.408
85.7	25	7	–	–	0.0556; 6 (n = 5)	0.571
126.5	25	7	–	–	0.0973	0.822
151.0	25	7	–	–	0.1173	0.900
85.7	25	7	–	–	0.0556; 6 (n = 5)	0.571
85.7	45	7	–	–	0.0624	0.598
85.7	55	7	–	–	0.0788	0.571
85.7	65	7	–	–	0.0912	0.608
85.7	25	3	–	–	0.0463; 2 (n = 3)	0.436
85.7	25	7	–	–	0.0556; 6 (n = 5)	0.571
85.7	25	10	–	–	0.1348; 4 (n = 3)	0.517
85.7	25	3	–	30.45	0.0417; 7 (n = 3)	0.369
85.7	25	7	–	30.45	0.0475; 5 (n = 3)	0.477
85.7	25	10	–	30.45	0.0890; 5 (n = 3)	0.514
85.7	25	7	10	–	0.0796	0.560
85.7	25	7	50	–	0.0815; 0.5 (n = 3)	0.550
85.7	25	7	100	–	0.0911; 0.3 (n = 3)	0.514
85.7	25	7	300	–	0.0778	0.536
85.7	25	7	600	–	0.0805	0.552
85.7	25	3	50	–	0.0679	0.408
85.7	25	7	50	–	0.0815; 0.5 (n = 3)	0.550
85.7	25	10	50	–	0.1126	0.528

[a] Corresponding to an ozone load of 1.63 to 7.55 μmol min^{-1} L_{water}^{-1}.

the BP3 rate constants increased from 0.0556 to 0.0912 min^{-1} at higher temperature, whereas no significant effect in the consumption of ozone was observed.

The reaction temperature may influence ozonation processes in two aspects. First, the Henry's law coefficient of ozone increases by more than a factor of 2 at higher temperature (25–65 °C) (Phattaranawik et al., 2005), limiting the mass transfer from gas to liquid phase and thus negatively affecting the BP3 degradation efficiency (see Section 3.2). Second, higher temperature may increase both the instability of ozone itself, as well as the activation of the reactive species leading to the enhancement of the BP3 degradation rate (Zhao et al., 2009). At the conditions applied in this study, it appears that the second temperature effect dominates the first one. Since the amount of ozone dissolved in the water phase is expected to be smaller at higher temperature, and given that the consumed amount of ozone is almost independent of temperature, it seems that a higher fraction of the available ozone is converted at higher temperature, which indicates a more efficient use of the aqueous ozone for direct or radicalar BP3 degradation.

3.4. pH effect

Since pH may affect both the ozonation rates and mechanistic pathways of organic micropollutants (Chelme-Ayala et al., 2011; Garoma and Matsumoto, 2009), the ozonation of BP3 was investigated at acid, neutral and alkaline conditions. Table 2 shows a clear increase of the BP3 removal rate at higher pH, particularly between pH 7 and pH 10. This can be explained by the higher rate of ozone decomposition at higher pH as the hydroxyl ions catalyze the decay of ozone to form hydroxyl radicals serving as reactive species (Hoigné and Bader, 1983). At pH 3, when no hydroxyl radical formation is expected and molecular ozone is presumed to be the most important reactive species, the decomposition of BP3 is slower than at neutral and basic conditions. This is also in agreement with Blüthgen et al. (2012) who noticed that benzophenone-derivatives (including BP3) are stabilized under acidic conditions. At pH 10, the BP3 decomposition rate is more than 2-fold higher than at acid pH, showing the importance of the formed hydroxyl radicals. The reactivity of BP3 with HO• is significantly higher than with aqueous ozone, as is the case with most organic compounds (Garoma and Matsumoto, 2009). Moreover, since BP3 has a pKa of 8.06, it is mainly dissociated at higher pH, which might result into an enhancement of the reaction rate since ozone is an electrophilic reagent.

Blank experiments showed an increase of ozone consumption with increasing pH, which can be explained by the enhanced mass transfer due to the chemical conversion of ozone into hydroxyl radicals keeping the driving force high. The quantity of ozone consumed during the first 60 min of ozone dosing in the blank experiments amounted 0.204, 0.278 and 0.513 mmol at pH 3, 7 and 10, respectively. When subtracting these amounts from those consumed during the BP3 degradation experiments, values of 0.232 mmol (pH 3), 0.292 mmol (pH 7) and 0.005 mmol (pH 10) are obtained. The fact that at pH 10 almost no extra consumption of ozone is observed in the presence of BP3 supports the dominating effect of the indirect BP3 degradation by formed radicals compared to the direct ozonation pathway. By dividing ozone net consumption by the amount of BP3 degraded in the same time interval, values of 4.32 (pH 3), 5.46 (pH 7) and 0.08 (pH 10) mmol of ozone consumed per mmol BP3 removed, are obtained. However, it should be considered that part of the ozone consumed is due to the formed intermediate products.

In order to better understand the role of hydroxyl radicals during BP3 ozonation, t-butanol (TBU) was added in excess (30.45 mM) at each investigated pH. TBU is a strong hydroxyl radical scavenger having reaction rates of 6×10^{8} M^{-1} s^{-1} with HO• (Buxton et al., 1988) and 3×10^{-3} M^{-1} s^{-1} with ozone (Hoigné and Bader, 1983). Fig. 2 illustrates the effect of TBU on the BP3 degradation at pH 3, 7 and 10. Although TBU addition increased the BP3 half-life time at each pH (10% at pH 3 and 16% at pH 7), the effect is most pronounced at pH 10 (51%). This is in agreement with the expected higher hydroxyl radical concentration at alkaline conditions. Moreover, given the small ozone consumption (0.005 mmol) attributed to BP3 degradation at pH 10 as noticed in the absence of TBU, the effect of TBU could have been

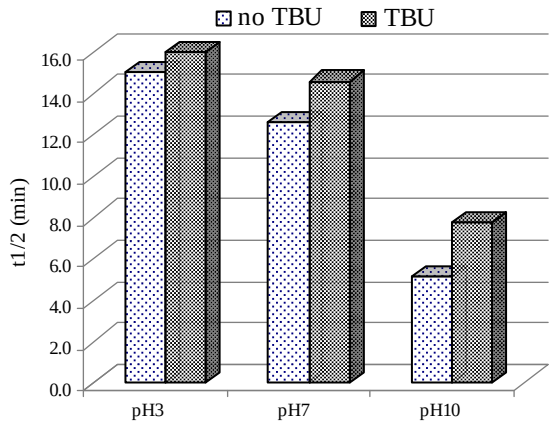

Fig. 2. Effect of t-butanol (TBU) on the BP3 half-life time during ozonation at an initial concentration of 22.3 μmol L^{-1}, 85.7 μmol L_{gas}^{-1} ozone inlet concentration, T = 25 °C, and at different values of pH.

expected to be even more pronounced. However, mass transfer aspects should also be taken into consideration. TBU addition is reported to yield smaller gas bubbles and thus higher interfacial area with the liquid phase, resulting into an increased k_La (Lopez-Lopez et al., 2007). Next to that, also the role of other reactive radicals, different from HO• might not be excluded.

3.5. O_3/H_2O_2 process

Given the relevance of hydroxyl radicals as shown in Section 3.4, peroxone experiments were performed at pH 7 by adding various H_2O_2 dosages (10 to 600 μmol L^{-1}) in the aqueous phase as a source for HO• generation in the O_3/H_2O_2 process. The degradation of BP3 by using O_3/H_2O_2 still followed the pseudo-first-order decay, and rate constants are shown in Table 2. Although not statistically significant, the H_2O_2 dosage influences the oxidation process rate. Differences are relatively low (<7% deviation from the mean value) in the 10–600 μmol L^{-1} range, but clearly higher than those observed when repeating three times the experiment at $[H_2O_2] = 100$ μmol L^{-1} (RSD = 0.3%). As a result of a promoted HO• radical formation (Gogate and Pandit, 2004), an increment of the BP3 degradation rate is observed as the H_2O_2 concentration increases, to reach a maximum ($k_{1,BP3}$ = 0.0911 min^{-1}) at 100 μmol L^{-1} H_2O_2, being 64% higher than without H_2O_2. At higher H_2O_2 dosages, however, the BP3 degradation rate decreased, showing similar values at 10 μmol L^{-1} H_2O_2 and 600 μmol L^{-1} H_2O_2. This inhibiting effect on the oxidation of BP3 may be explained by the scavenging behavior of H_2O_2 towards hydroxyl radicals (Chu and Lau, 2007; Yasunaga et al., 2006; De Witte et al., 2009). The ozone consumption as a function of H_2O_2 concentration followed an opposite trend to that of the BP3 degradation rate. The lowest ozone consumption was measured at 100 μmol L^{-1} H_2O_2 (Table 2), i.e. at the maximum BP3 removal rate. This fact may be attributed to the higher concentration of radicals present in the aqueous phase, reducing the ozone consumption due to direct reaction with BP3.

The effect of pH (3, 7, 10) was also studied in the peroxone process (Table 2). Adding 50 μmol L^{-1} H_2O_2 in the aqueous solution did increase the BP3 removal rate by 47% at pH 3, which is completely in line with the results obtained at neutral pH. In contrast, the BP3 degradation at pH 10 was almost 20% slower when H_2O_2 was added. Since in this case high concentrations of hydroxyl radicals and H_2O_2 are present simultaneously, the observed rate retardation most probably results from the consumption/scavenging of hydroxyl radicals by H_2O_2, yielding less reactive radicals (such as HO_2•) in the solution (Sun and Pignatello, 1992; Poulopoulos et al., 2006).

3.6. Ozonation byproduct identification

Table 3, summarizes for all major peaks detected during HPLC–QTOF-MS/MS analysis the retention time, the exact mass and elemental formula of both the molecular and fragment ions. It also lists the calculated mass errors and double bond equivalents (DBEs) of the proposed reaction products formed during BP3 ozonation. These data were obtained under optimized conditions of collision energy and cone voltage in both ESI(+)- and ESI(−)-MS/MS experiments. Since almost all fragment ions had an even number of electrons (as exemplified by half-integer DBE values), most of the neutral losses had likewise even electron configurations. Fig. S1 (Supplementary information) shows the HPLC–ESI-MS/MS chromatograms of BP3 and its formed ozonation products.

Fig. 3a–e shows the ESI(+)-MS/MS product ion spectra of the detected compounds. The CID fragmentation of BP3 (molecular ion $[M+H]^+$ 229), which elutes at 8.51 min, shows the split of the molecule to leave the positive charge in the keto group that is resonantly stabilized by the adjacent aromatic ring. The fragment at m/z 151 is produced by the loss of the phenyl group of BP3 $[M-C_6H_5]^+$, whereas the fragment at m/z 105 corresponds to the benzoyl cation $[C_6H_5C{=}O]^+$. Apart from BP3, 5 other chromatographic peaks were observed during ESI(+) full scan analysis of samples collected during the first 25 min of BP3 ozonation at standard conditions. Four peaks with a molecular ion $[M+H]^+$ 245 were observed at 7.88, 6.93 and 6.82 min (ozonation byproduct m/z 244a (Pr244a)) and 6.50 min (ozonation byproduct m/z 244b (Pr244b)). Considering that the mass of these compounds is shifted 16 Da upwards relative to the parent compound, hydroxylation by HO• attack is the most plausible explanation. The peaks at 7.88, 6.93 and 6.82 min show an identical fragmentation pathway in the ESI(+)-MS/MS experiments (Fig. 3b), with clear similarities with the MS/MS spectra obtained for BP3. Indeed, the same fragment at m/z 151 is formed, and instead of the fragment at m/z 105 (BP3), a fragment at m/z 121 (+16 Da) is detected for Pr244a. In light of these results, it appears that BP3 has been hydroxylated in the unsubstituted aromatic ring of the molecule as a consequence of a non-specific HO• attack. The three peaks represent the ortho-, meta- and para-hydroxylated forms. The peak at 7.88 min (ortho position) corresponds to DHMB, as confirmed by the analysis of a commercial analytical standard solution. The peak at 6.50 min (Pr 244b) also having the molecular ion at $[M+H]^+$ 245 (Fig. 3c) results from the hydroxylation of BP3 at the other moiety of the molecule. This is supported by the fragment at m/z 167 instead of m/z 151 and by the presence of the fragment at m/z 105. The fifth peak (ozonation byproduct m/z 214, (Pr214)) detected already after 5 min of BP3 ozonation, elutes at 6.78 min and corresponds to the molecular ion $[M+H]^+$ 215. ESI(+)-MS/MS spectra show two fragments (Fig. 3d), one at m/z 105 (the same as that observed for BP3, $[C_6H_5{=}O]^+$) and another one at m/z 137 $[M-C_6H_5]^+$. The difference in mass (14 Da) with the $[M-C_6H_5]^+$ ion of BP3 strongly suggests demethylation of BP3. The resulting molecule corresponds to BP1, which is also a commonly used UV filter compound and whose identity was confirmed by the analysis of a commercial analytical standard. After 15 min of BP3 ozonation, a sixth peak occurred in the ESI(+) full scan analysis, eluting at 5.13 min (ozonation byproduct m/z 258 (Pr258)). From the ESI(+)-MS/MS spectra and the structures proposed for the fragments (Fig. 3e), it is highly probable that Pr258, having a molecular ion 14 Da higher in mass than Pr244b, is formed through the oxidation of the methyl group in Pr244b converting it to an aldehyde functionality.

At the same conditions, ozonated samples collected as a function of time were also analyzed by ESI(−)-MS/MS full scan analysis. For the products Pr244a, Pr244b and Pr214 (BP1), corresponding peaks were detected at the same retention time as obtained in ESI(+) analysis (Table 3). In the case of BP1, CID fragments in ESI(−) were obtained at m/z 135, 109 and 91 (Fig. 3f). Similar results were obtained for DHMB in the negative mode (results not shown), being in agreement

Table 3
Retention time, accurate mass measurement and elemental formula of the molecular and fragment ions of both benzophenone-3 (BP3) and its ozonation degradation products, as elucidated by HPLC-QqTOF analysis in both ESI(+) and ESI(−) ionization modes.

t_R[a] (min)	Compound	Precursor and production	Elemental formula	Mass (m/z)		Error		DBE[b,c]
				Experimental	Theoretical	mDa	ppm	
8.51	BP3	$[M+H]^+$	$C_{14}H_{13}O_3$	229.0870	229.0865	0.5	2.2	8.5
		$[M-C_6H_5]^+$	$C_8H_7O_3$	151.0399	151.0395	0.4	2.6	5.5
		$[C_6H_5{=}O]^+$	C_7H_5O	105.0346	105.0340	0.6	5.7	5.5
7.88, 6.93, 6.82	Pr244a	$[M+H]^+$	$C_{14}H_{13}O_4$	245.0812	245.0814	−0.2	−0.8	8.5
		$[M-C_6H_5OH]^+$	$C_8H_7O_3$	151.0400	151.0395	0.5	3.3	5.5
		$[C_6H_4(OH){=}O]^+$	$C_7H_5O_2$	121.0294	121.0290	0.4	3.3	5.5
		$[M-H]^-$	$C_{14}H_{11}O_4$	243.0650	243.0657	−0.7	−2.9	9.5
		$[M-CH_3]^-$	$C_{13}H_8O_4$	228.0412	228.0423	−1-1	−4.8	10
		$[C_6H_4(OMe)O]^-$	$C_7H_7O_2$	123.0452	123.0446	0.6	4.9	4.5
		$[C_6H_5O]^-$	C_6H_5O	93.0335	93.0340	−0.5	−5.4	4.5
6.50	Pr244b	$[M+H]^+$	$C_{14}H_{13}O_4$	245.0812	245.0814	−0.2	−0.8	8.5
		$[M-C_6H_5]^+$	$C_8H_7O_4$	167.0349	167.0344	0.5	3.0	5.5
		$[C_6H_5{=}O]^+$	C_7H_5O	105.0338	105.0340	−0.2	−1.9	5.5
		$[M-H]^-$	$C_{14}H_{11}O_4$	243.0648	243.0657	−0.9	−3.7	9.5
		$[M-CH_3]^-$	$C_{13}H_8O_4$	228.0424	228.0423	0.1	0.4	10
		$[C_6H_4(OMe)(OH)O]^-$	$C_7H_7O_3$	139.0389	139.0395	−0.6	−4.3	4.5
6.78	Pr214	$[M+H]^+$	$C_{13}H_{11}O_3$	215.0710	215.0708	0.2	0.9	8.5
		$[M-C_6H_5]^+$	$C_7H_5O_3$	137.0241	137.0239	0.2	1.5	5.5
		$[C_6H_5{=}O]^+$	C_7H_5O	105.0345	105.0340	0.5	4.8	5.5
		$[M-H]^-$	$C_{11}H_9O_3$	213.0549	213.0552	−0.3	−1.4	9.5
		$[C_6H_3(O)_2C{=}O]^{\bullet\bullet-}$	$C_7H_3O_3$	135.0079	135.0082	−0.3	−2.2	6.5
		$[C_6H_5(OH)O]^-$	$C_6H_5O_2$	109.0290	109.0290	0	0	4.5
		$[C_6H_3O]^{\bullet\bullet-}$	C_6H_3O	91.0180	91.0184	−0.4	−4.4	5.5
5.13	Pr258	$[M+H]^+$	$C_{14}H_{11}O_5$	259.0597	259.0606	−0.9	−3.5	9.5
		$[M-C_6H_5]^+$	$C_8H_5O_5$	181.0136	181.0137	−0.1	−0.6	6.5
		$[M-C_6H_5-C{=}O]^+$	$C_7H_5O_4$	153.0184	153.0188	−0.4	−2.6	5.5
		$[C_6H_5{=}O]^+$	C_7H_5O	105.0345	105.0340	0.5	4.8	5.5
6.34*	Pr260a	$[M-H]^-$	$C_{14}H_{11}O_5$	259.0601	259.0606	−0.5	−1.9	9.5
		$[C_6H_4(OMe)O]^-$	$C_7H_7O_2$	123.0452	123.0446	0.6	4.9	4.5
		$[C_6H_5(OH)O]^-$	$C_6H_5O_2$	109.0286	109.0290	−0.4	−3.7	4.5
		$[M-CH_3]^-$	$C_{13}H_8O_5$	244.0365	244.0372	−0.7	−2.9	10
5.12*	Pr260b	$[M-H]^-$	$C_{14}H_{11}O_5$	259.0612	259.0606	0.6	2.3	9.5
		$[M-CH_3]^-$	$C_{13}H_8O_5$	244.0362	244.0372	−1.0	−4.1	10
		$[C_6H_4(OMe)(OH)O]^-$	$C_7H_7O_3$	139.0390	139.0395	−0.5	−3.6	4.5
		$[C_6H_5O]^-$	C_6H_5O	93.0344	93.0340	0.4	4.3	4.5
6.13, 5.61, 5.31	Pr230	$[M-H]^-$	$C_{13}H_9O_4$	229.0496	229.0501	−0.5	−2.2	9.5
		$[C_6H_3(O)_2C{=}O]^{\bullet\bullet-}$	$C_7H_3O_3$	135.0077	135.0082	−0.5	−3.7	6.5
		$[C_6H_5(OH)O]^-$	$C_6H_5O_2$	109.0285	109.0290	−0.5	−4.6	4.5
		$[C_6H_5O]^-$	C_6H_5O	93.0337	93.0340	−0.3	−3.2	4.5
		$[C_6H_3O]^{\bullet\bullet-}$	C_6H_3O	91.0184	91.0184	0	0	5.5

[a] t_R: HPLC retention time.
[b] DBE: double bond equivalent.
[c] Several peaks around this time.

with Negreira et al. (2009). Next to that, the ESI(−)-MS/MS full scan analysis showed one group of peaks around 6.34 min (ozonation byproduct m/z 260a (Pr260a)) and another one around 5.12 min (ozonation byproduct m/z 260b (Pr260b)), both with the molecular ion $[M-H]^-$ 259. All the peaks of the first and second group show the same fragmentation pattern, given in Fig. 3g and h, respectively. The mass of the molecular ion is 16 Da upwards relative to Pr244a and Pr244b, so that the most probable explanation is another non-specific HO• oxidation of these compounds. After 20 min of ozonation, three additional peaks were observed in ESI(−), eluting at 6.13, 5.61 and 5.31 min (ozonation byproduct m/z 230 (Pr230)). The mass of the molecular ion is 16 Da upwards relative to Pr214, and the same fragmentation pathway is observed for the three peaks (Fig. 3i). Given the similarity with the ESI(−)-MS/MS spectra of BP1, it is suggested that Pr230 represents the ortho-, meta- and para-hydroxylation products of BP1 resulting from a HO• attack in the non-hydroxylated moiety of the molecule. The peak at 6.13 min (ortho position) corresponds to THB, as confirmed by the analysis of a commercial analytical standard solution.

Among the identified intermediate products, the commercially available BP1, DHMB and THB compounds have also been identified as BP3 degradation products or metabolites in other studies dealing with rats, human urine or fungal degradation (Gago-Ferrero et al., 2012b; Felix et al., 1998; Jeon et al., 2008). In order to obtain a quantitative profile of their formation/elimination during BP3 ozonation (Fig. 4), these compounds were measured in non-preconcentrated aqueous samples via HPLC–MS/MS SRM analysis (Section 2.3). BP1 and DHMB concentrations reach their maxima (0.055 and 0.047 μmol L^{-1} respectively) at about 15 min, to drop below the detection limit after 40 min of BP3 ozonation. Based on the integrated areas below the curves presented in Fig. 4, it can be estimated that of the total amount of BP1 degraded during the first 40 min of ozonation, about 0.5% was detected as BP1 and DHMB. THB was not detected in the non-preconcentrated samples. A supporting experiment, investigating BP1 ozonation at pH 7 in the same reactor and at the standard conditions (Section 2.2), revealed that BP1 (23.3 μmol L^{-1}; 5 mg L^{-1}) ozonation is slower than that of BP3, as exemplified by a half life time of 16.1 min (n = 3), compared to 12.6 min for BP3. This slower BP1 degradation supports its temporary accumulation during BP3 ozonation. Although the detected concentrations of BP1 are relatively low compared to the initial BP3 concentration, its formation should be taken into account when considering the application of ozonation for BP3 removal from wastewater. Since yeast based bioassay (ER-RYA) analysis showed that BP1 is about 200 times more estrogenic than its parental compound BP3, and three orders of magnitude less estrogenic than 17β-estradiol (Gago-Ferrero et al., 2012b), the ozonation time should

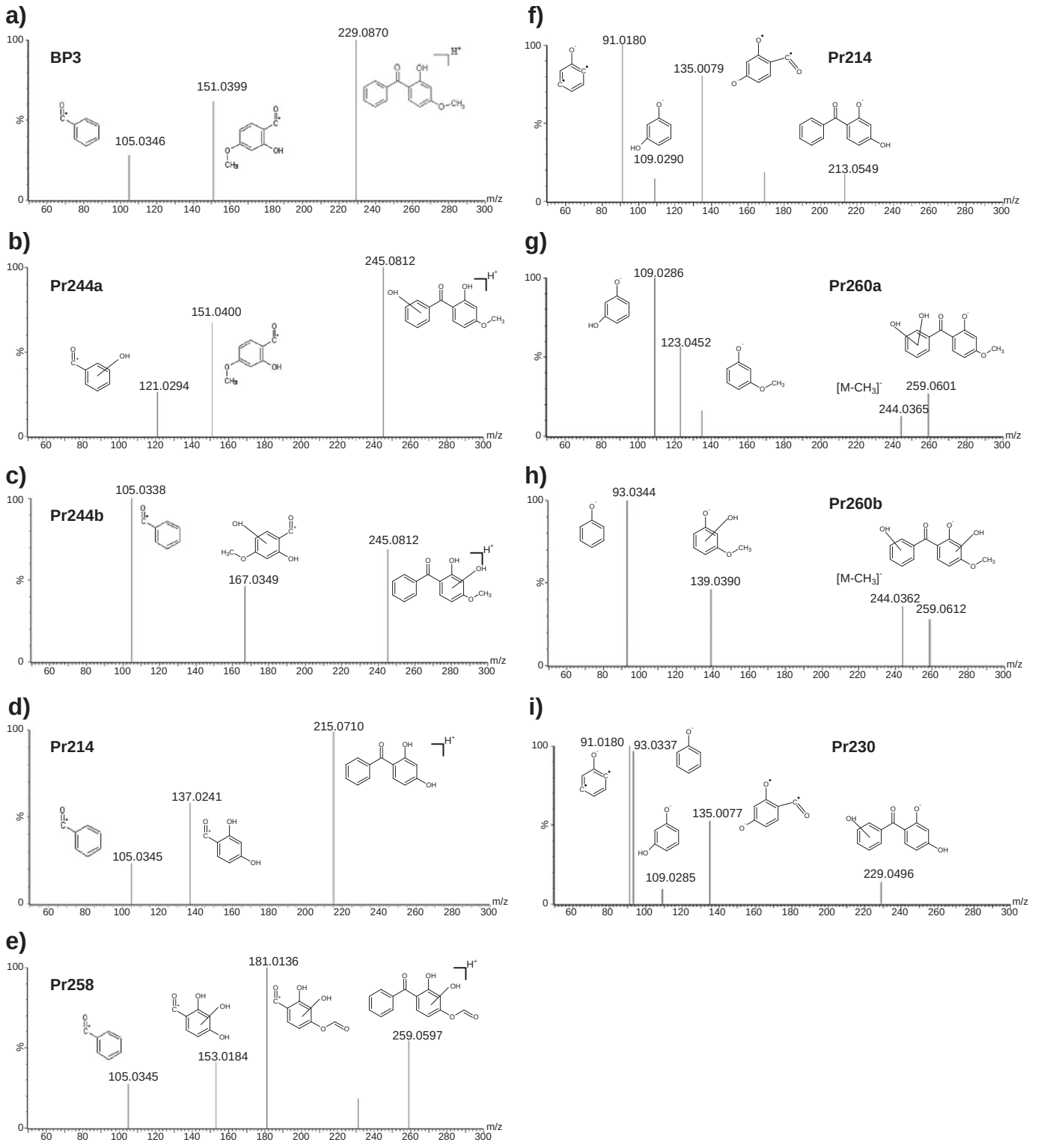

Fig. 3. Spectra obtained from full-scan ESI-QqTOF-MS/MS analysis of BP3 and its detected ozonation products. ESI(+)-MS/MS: (a) BP3, (b) Pr244a, (c) Pr244b, (d) Pr214 (BP1), and (e) Pr258. ESI(−)-MS/MS: (f) Pr214 (BP1), (g) Pr260a, (h) Pr260b, and (i) Pr230.

be long enough in order to remove both BP3 and BP1 from the reaction medium.

The fact that both BP1 and DHMB show a similar concentration profile, rising from the first minutes of ozonation, strongly indicates that both compounds are formed directly out of BP3, independently from each other. This is shown in Fig. 5, proposing the first steps in the BP3 ozonation pathways. The involvement of hydroxyl radicals in these pathways is further exemplified by byproduct identification analysis performed at the other pH values. During ozonation at pH 10 and during the peroxone experiments, the same hydroxylated degradation products were detected. DHMB concentrations were, however, up to 100% higher than at pH 7 and reached their maximum at already 6 min while the BP1 maximum kept similar to pH 7 experiments. By contrast, at pH 3, when direct ozonation is expected to be

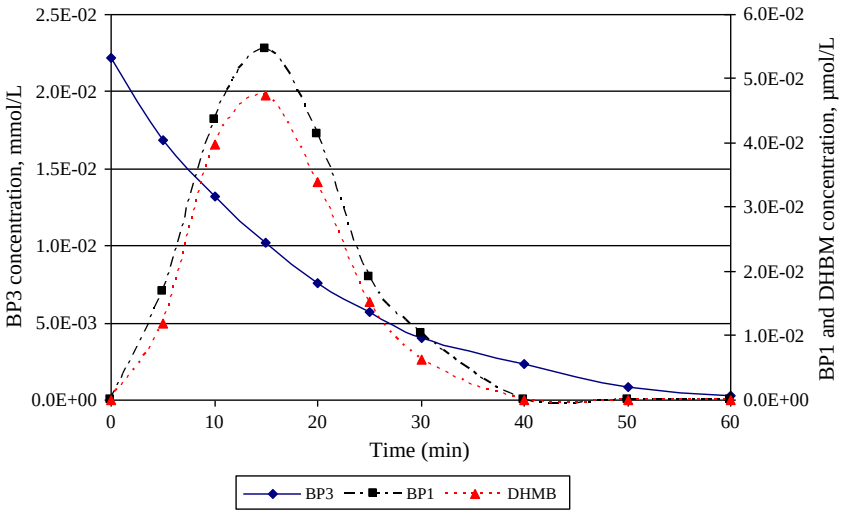

Fig. 4. BP3, DHMB and BP1 concentration profiles measured during BP3 ozonation at standard conditions (85.7 µmol L_{gas}^{-1} O_3, 25 °C, pH 7).

one of the major reaction pathways, maximum concentrations achieved for DHMB and BP1 are respectively 80% and 20% lower than those obtained at pH 10, and maximum concentrations were reached at 20 min for both compounds.

4. Conclusions

This study brings forward new data and insights with respect to both the effect of operational variables (ozone inlet gas concentration, temperature, pH, and H_2O_2 addition) on and reaction pathways of benzophenone-3 ozonation in water. A major conclusion is that process conditions that favor hydroxyl radical formation have a pronounced positive effect on BP3 degradation, which shows the higher reactivity through radicalar pathways compared to direct ozonation. Through advanced LC-MS/MS analysis, up to 7 BP3 ozonation intermediate products could be identified and structurally characterized. As far as we know, this is the first study providing data on the identification of BP3 ozonation byproducts. Apart from benzophenone-1 (BP1), which is a result of

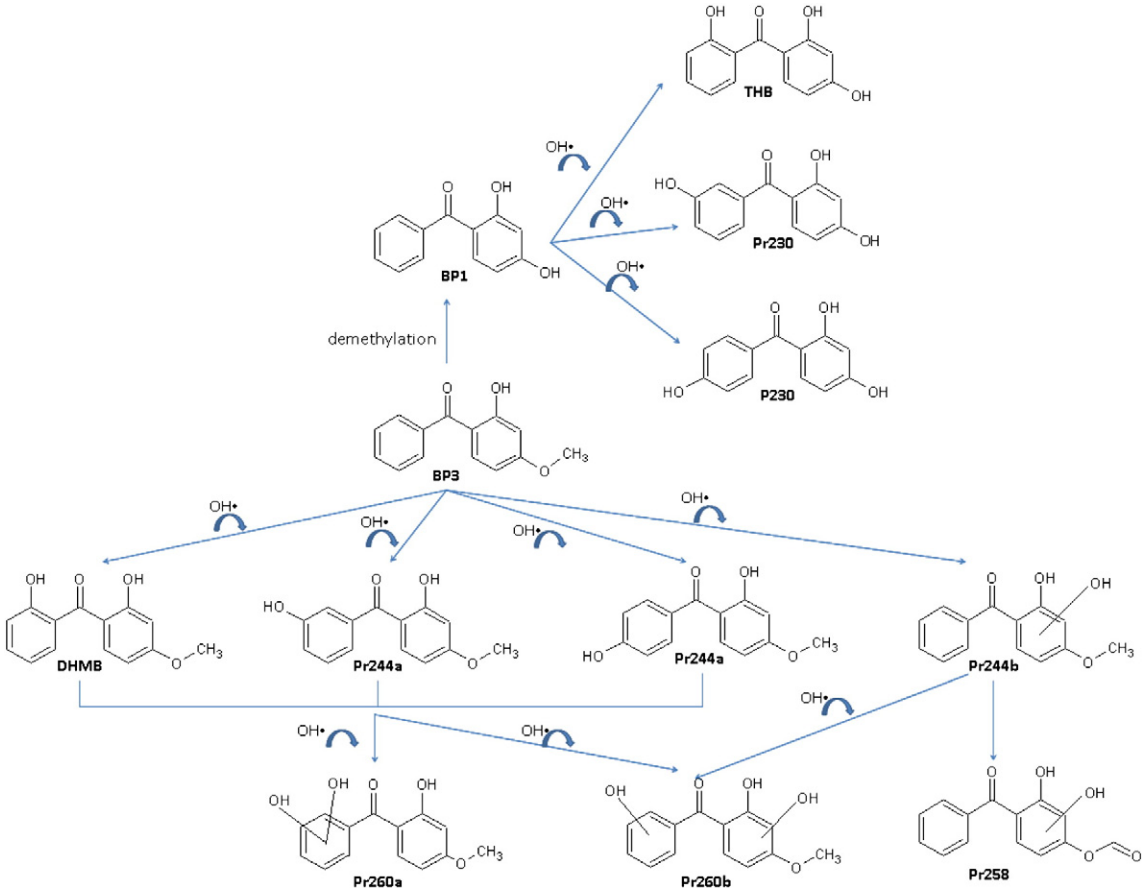

Fig. 5. Proposed initial degradation pathways of BP3 during ozonation in aqueous solution at standard conditions (85.7 µmol L_{gas}^{-1} O_3, 25 °C, pH 7).

BP3 demethylation, all other identified degradation products were hydroxylated derivatives, formed by a non-specific attack of HO• radicals at different moieties of the molecule.

Since this work – as being one of the first on this topic – has been performed in deionized water at relatively high concentrations, the results should be interpreted within its context and goal of this work, and might not be quantitatively transferable to real conditions. However, the acquired knowledge is of the utmost use to better understand the process and to further investigate the application potential of ozonation for UV-filter removal in real environmental or wastewaters. In order to avoid the introduction of estrogenic activity in the aquatic environment, the focus should not only be put on the removal of the parent compound but also the further oxidation of harmful reaction products like BP1 is certainly a topic for a more in-depth study.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.10.006.

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