



Significant role of UV and carbonate radical on the degradation of oxytetracycline in UV-AOPs: Kinetics and mechanism



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ABSTRACT

Carbonate radical ($\text{CO}_3^{\bullet-}$), a selective oxidant, reacts readily with electron-rich compounds through electron transfer and/or hydrogen abstraction. In this study, the role of $\text{CO}_3^{\bullet-}$ in degrading oxytetracycline (OTC) by UV only, UV/ H_2O_2 and UV/persulfate (UV/PS) advanced oxidation processes (AOPs) in the presence of HCO_3^- or CO_3^{2-} was investigated. For UV only process, the presence of photosensitizers, i.e., nitrate (NO_3^-) and natural organic matter (NOM), had different impacts on OTC degradation, i.e., an enhancing effect by NO_3^- due to the generation of HO^\bullet and a slight inhibiting effect by NOM possibly due to a light scattering effect. Differently for UV/ H_2O_2 and UV/PS processes, the presence of NO_3^- hardly influenced the destruction of OTC. Generation of $\text{CO}_3^{\bullet-}$ presented a positive role on OTC degradation by UV/ $\text{NO}_3^-/\text{HCO}_3^-$. Such influence was also observed in the two studied AOPs in the presence of both bicarbonate and other natural water constituents. When various natural water samples from different sources were used as reaction matrices, UV only and UV/ H_2O_2 showed an inhibiting effect while UV/PS demonstrated a comparable or even promoting effect in OTC decomposition. After elucidating the potential contribution of UV direct photolysis via excited state OTC^* at an elevated reaction pH condition, putative OTC transformation byproducts via $\text{CO}_3^{\bullet-}$ reaction were identified by ultra-high definition accurate-mass quadrupole time-of-flight tandem mass spectrometry (QTOF/MS). Five different reaction pathways were subsequently proposed, including hydroxylation (+16 Da), quinonization (+14 Da), demethylation (−14 Da), decarbonylation (−28 Da) and dehydration (−18 Da). The significant role of UV at high pH and $\text{CO}_3^{\bullet-}$ on OTC removal from contaminated water was therefore demonstrated both kinetically and mechanistically.

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1. Introduction

Tetracyclines (TCs) are an important class of broad-spectrum antibiotics that have been extensively used not only for disease prevention but also as growth promoters in livestock (Kemper, 2008; Sarmah et al., 2006). Most TCs are excreted unmetabolized through urine and feces because of poor absorption (Kemper, 2008;

Kümmerer, 2009a). Accordingly, they have been frequently detected in different environmental compartments, e.g., surface water, sewage water, groundwater, seawater, and sediment, throughout the world (Hirsch et al., 1999; Kemper, 2008; Kümmerer, 2009a; Michael et al., 2013; Sarmah et al., 2006). The occurrence of TCs in the environment may induce a potential risk to human health and ecosystem through the development of antibiotic resistant bacteria or pathogens (Auerbach et al., 2007; Kümmerer, 2009b; Rizzo et al., 2013; Sarmah et al., 2006). Therefore, TCs have been recognized as contaminants of emerging concern (CECs) and are gaining significant public attention and scientific interest in recent years (Hirsch et al., 1999; Kemper, 2008; Kümmerer, 2009a, 2009b). Oxytetracycline (OTC), a common member of TCs, is often chosen as a model compound to investigate the removal of TCs from the

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contaminated aquatic systems. Due to its chemical stability and antibiotic property, conventional water treatment technologies, such as biodegradation and chlorination, are not efficient for OTC destruction (Watkinson et al., 2007). Advanced oxidation processes (AOPs), such as ozonation, photocatalysis, UV-254 nm/H₂O₂ and UV-254 nm/persulfate (PS), are thus proposed as promising alternative methods to remove OTC (Li et al., 2008; Liu et al., 2015, 2016a, 2016b; Yuan et al., 2011; Zhao et al., 2010).

Carbonate radical (CO₃^{•-}) is a selective one-electron oxidant (E₀ = 1.78 V at pH 7) and has varied reactivity towards organic compounds (10²–10⁹ M⁻¹ s⁻¹) (Mazellier et al., 2007; Neta et al., 1988). As an electrophilic radical species, CO₃^{•-} reacts mainly with electron-rich compounds, such as N-containing organics, S-containing organics, and phenols, through electron transfer or hydrogen abstraction (Neta et al., 1988; Wu and Linden, 2010). Currently, generation of CO₃^{•-} has been reported by several pathways including direct photodecomposition of carbonatoamine complexes of cobalt (III) and reaction of either carbonate or bicarbonate with hydroxyl radical (HO[•]), sulfate radical (SO₄^{•-}) or excited state aromatic ketones (Canonica et al., 2005; Cope et al., 1973; Mazellier et al., 2007). Recently, Zhang et al. (2015b) reported that the much higher concentration of CO₃^{•-} (four and two orders of magnitude greater than HO[•] and SO₄^{•-}, respectively) could be generated in UV/H₂O₂ and UV/PS systems in the presence of bicarbonate. In natural waters, CO₃^{•-} can be generated through the oxidation of bicarbonate or carbonate with HO[•] that are formed by the photolysis of nitrate, nitrite and natural organic matter (NOM) and/or by photo-Fenton reactions (Huang and Mabury, 2000). The steady-state concentration of CO₃^{•-} has been estimated to be two orders of magnitude higher than that of HO[•] in sunlit surface waters (Canonica et al., 2005; Huang and Mabury, 2000). Therefore, the role of CO₃^{•-} can not be negligible in removing organic contaminants, especially those with electron-rich moieties such as OTC which has a reported second-order rate constant of 2.9 × 10⁸ M⁻¹ s⁻¹ with CO₃^{•-} (Liu et al., 2015). Consequently, CO₃^{•-} has received increasing attention recently (Dell'Arciprete et al., 2012; Vione et al., 2009) although its reaction towards organic contaminants is still limitedly studied.

In our previous work (Liu et al., 2015, 2016a), an enhancement was observed in the destruction of OTC by UV/H₂O₂ and UV/PS in the presence of either carbonate or bicarbonate, which was confirmed to be due to the positive role of CO₃^{•-}. However, the degradation mechanism of OTC by CO₃^{•-} is still unknown. The main objective of this study was thus to investigate the probable transformation pathways of OTC by CO₃^{•-} based on the identified reaction byproducts aiming to better understand the significant contribution of CO₃^{•-} in the degradation of OTC. In addition, the potential role of UV in such CO₃^{•-} based systems on the degradation and transformation of OTC was studied. The influence of photosensitizers, e.g., nitrate (NO₃⁻) and NOM, on the degradation of OTC by UV only, UV/H₂O₂ and UV/PS AOPs was also evaluated. Finally, the removal of OTC using natural water samples from different origins as a reaction matrix was explored to assess the potential application of these technologies on OTC treatment. To the best of our knowledge, this is the first study to investigate the degradation mechanism of OTC by UV at high pH and by CO₃^{•-}.

2. Materials and methods

2.1. Materials

Oxytetracycline hydrochloride (>95%) and sodium persulfate (98%, Na₂S₂O₈) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Hydrogen peroxide (50 wt%) and potassium nitrate (≥99%, KNO₃) were purchased from Fisher Scientific (Pittsburgh, PA, USA).

Suwannee River humic acid (HA) and fulvic acid (FA) standards were obtained from International Humic Substances Society (IHSS, University of Minnesota, St. Paul, MN, USA) and used for representing NOM. Other chemicals, such as sodium bicarbonate (NaHCO₃), sodium chloride (NaCl), and cupric sulfate pentahydrate (CuSO₄ · 5H₂O) were all ACS grade and used as received. Natural water samples collected at different locations were applied as reaction matrices for a specific series of experiments. General water quality parameters, such as pH, alkalinity, total organic carbon (TOC), and UV–Vis absorbance at 254 nm, are presented in Table 1.

2.2. Analysis

The concentration of OTC was quantified by a high performance liquid chromatograph (HPLC, Agilent 1100 Series). A C₁₈ Discovery HS (Supelco) column (4.6 × 150 mm, 5 μm) was applied as a stationary phase. The mobile phase consisted of 0.005 M oxalic acid water solution/methanol/acetonitrile (60/20/20, v/v/v) with a flow rate of 0.4 mL min⁻¹. The detection wavelength was 355 nm, with a column temperature of 35 °C and a sample injection volume of 20 μL. The reaction byproducts were detected and identified by an Agilent 6540 ultra-high definition accurate-mass quadrupole time-of-flight tandem mass spectrometer (QTOF/MS) coupled with an Agilent 1290 infinity HPLC system (LC-QTOF/MS). The detailed analytical method can be found elsewhere (Liu et al., 2016b). The QTOF scan data were analyzed using Agilent MassHunter B.04.00 workstation software. Alkalinity was measured by the AWWA Standard Method (Eaton et al., 1995). TOC was determined by a Shimadzu VCSH-ASI TOC Analyzer. UV–Vis absorbance was analyzed by a Hewlett Packard UV–Vis spectrophotometer. Specific UV absorbance at 254 nm (SUVA₂₅₄) was calculated based on EPA Method 415.3 (Potter and Wimsatt, 2005).

2.3. Photochemical experiments

The irradiation experiments were carried out in a bench scale collimated beam system where two low pressure Hg UV lamps (15 W, Cole-Parmer) with primary monochromatic emission of λ_{max} = 254 nm were used. The average UV fluence rate was measured to be 0.1 mW cm⁻² by three different methods (He et al., 2012). For OTC destruction experiments, the initial concentration of OTC was 10 μM (4.6 mg L⁻¹), unless stated otherwise. The degradation of OTC could be enhanced with increasing pH in UV only system; while in UV/H₂O₂ and UV/PS systems, the k_{obs} was the highest at pH 5.5 and at near neutral pH conditions (pH 5.5–8.5), respectively (Liu et al., 2015, 2016a). Therefore, to minimize the impact of pH, the degradation of OTC with the addition of water constituents in phosphate buffer solution (50 mM) was used as the respective controls. For example, as compared to those in the presence of 6 mM NaHCO₃ (pH = 9.0) and 3 mM NaHCO₃ (pH = 8.5), the pH of 50 mM phosphate buffer was adjusted to 9.0 and 8.5, respectively, in the control series. All other degradation experiments in the absence of NaHCO₃ were performed in Milli-Q water (pH = 5.8). At given UV fluence, 0.15 mL of reaction solution was taken and mixed with 0.1 mL 0.05 N Na₂S₂O₃ in the UV/H₂O₂ and UV/PS systems, while the irradiated solution was sampled without adding any quenching agent in the UV only system prior to HPLC analysis. For OTC degradation mechanism investigation, a higher initial OTC concentration of 40 μM (18.4 mg L⁻¹) was applied. At various given times, the sample was taken and analyzed immediately. No quenching agent was used in this process to limit its influence on the detection of degradation byproducts. All experiments were performed in triplicate except for the mechanism study. The error bars in the figures represent the standard error of the mean.

Table 1

Water quality parameters measured after sample filtration by a 0.45 µm filter.

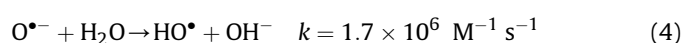
	pH	Total alkalinity (mg L ⁻¹ CaCO ₃)	TOC (mg L ⁻¹)	UV–Vis absorbance @ 254 nm	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)
GCWW-1	7.54	58	2.96	0.0790	2.67
GCWW-2	7.57	49	1.85	0.0434	2.35
GCWW-3	7.75	49	1.62	0.0339	2.09
GCWW-4	7.64	50	1.27	0.0161	1.27
GCWW-5	7.77	52	1.14	0.0139	1.22
GL	7.55	236	7.05	0.122	1.73
LK	8.60	724	36.85	0.383	1.04
LH-1	7.22	140	7.76	0.263	3.39
LH-2	7.70	176	7.70	0.140	1.82
SJR	8.35	1588	94.68	1.32	1.39

Abbreviation: GCWW: Greater Cincinnati Water Works, March 31, 2015; 1, 2, 3, 4 and 5 representing samples of raw water from Ohio River, before sand filtration, before granular activated carbon (GAC), after GAC and effluent from GCWW, respectively. GL: Grand Lake, Ohio, July 19, 2013; LK: Lake Karla, Greece, September 23, 2014; LH-1 and LH-2: Lake Harsha, Ohio, March 27, 2015; SJR: St. Johns River, Florida, March 27, 2015.

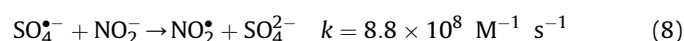
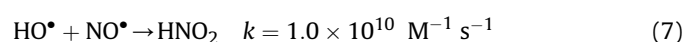
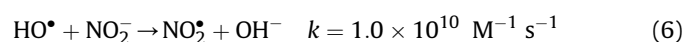
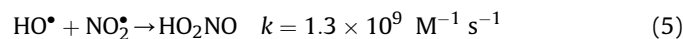
3. Results and discussion

3.1. Effect of photosensitizers, i.e., NO₃⁻ and/or NOM

The influence of the two common photosensitizers, i.e., NO₃⁻ and NOM, on the destruction of organic pollutants under (simulated) sunlight irradiation has been studied extensively during the last decades (Chen et al., 2009; Yu et al., 2010; Zepp et al., 1987). Generally, NOM exhibits two opposite effects: (1) a promoting effect caused by the generated triplet excited state NOM and/or reactive oxygen species (ROS) such as HO•, ¹O₂, and O₂^{•-}; and (2) an inhibiting effect because of its light screening and/or radical scavenging effects (Canonica, 2007; Carlos et al., 2012; Vaughan and Blough, 1998; Xu et al., 2011). As shown in Fig. 1a, the observed UV fluence-based pseudo first-order rate constant of OTC (*k*_{obs}) decreased slightly in the presence of different concentrations of HA or FA, suggesting that the contribution of effect (2) exceeded that of effect (1) for NOM in the UV direct photolysis of OTC. In contrast, the *k*_{obs} was enhanced with the addition of NO₃⁻ and became higher at a higher concentration of NO₃⁻ (Fig. 1a). This was probably due to the generation of HO• by the excited NO₃⁻, as shown in Eqs. (1)–(4) (Keen et al., 2012; Mack and Bolton, 1999; Mark et al., 1996). To further confirm this speculation, 10 mM methanol (MeOH, *k*_{HO•/MeOH} = 9.7 × 10⁸ M⁻¹ s⁻¹ (Buxton et al., 1988)) or 50 mM isopropanol (i-PrOH, *k*_{HO•/i-PrOH} = 1.9 × 10⁹ M⁻¹ s⁻¹ (Buxton et al., 1988)), two well-known HO• scavengers, was added into the reaction solutions. The results are presented in Fig. S1 in supporting information (SI). The degradation of OTC after the addition of NO₃⁻ and MeOH or i-PrOH was almost the same as that in Milli-Q water only condition, well demonstrating the aforementioned explanation. Accordingly, due to the presence of HO• in the UV-254 nm irradiated KNO₃ solution, the OTC degradation was improved in the presence of both NO₃⁻ and NOM compared with that in the presence of only NOM (Fig. 1a and b). Yet, due to the UV light absorption and/or HO• scavenging of NOM (*k*_{HO•/NOM} = 2.23 × 10⁸ L (mol C)⁻¹ s⁻¹ (Westerhoff et al., 2007)), an inhibiting effect of HA or FA on the removal of OTC was still observed by comparing UV/NO₃⁻/NOM to UV/NO₃⁻, as shown in Fig. 1b.

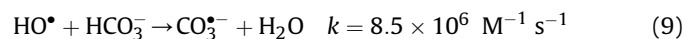


Though NO₃⁻ had a positive effect on the degradation of OTC by UV only process, no significant influence was observed in the UV/H₂O₂ or UV/PS process, as depicted in Fig. 1c. In addition to the high radical quantum yields of H₂O₂ and PS under UV-254 nm activation (Baxendale and Wilson, 1957; Mark et al., 1990), HO• and SO₄^{•-} could react with the NO₃⁻ photolysis intermediates, such as NO₂^{*}, NO₂⁻ and NO•, as shown in Eqs. (5)–(8) (Buxton et al., 1988; Keen et al., 2012; Mack and Bolton, 1999; Neta et al., 1988) and therefore, the contribution of HO• generated by the activated NO₃⁻ might be insignificant. Similar findings were also reported by Tan et al. (2013) in the degradation of antipyrine by UV only, UV/H₂O₂ and UV/PS.



3.2. Effect of carbonate radical

CO₃^{•-} can be generated by the reaction of HO• with NaHCO₃ (Eq. (9) (Buxton et al., 1988)) to enhance the degradation of OTC by UV/H₂O₂ (Liu et al., 2015). Therefore, with the presence of HO• being demonstrated above in UV/NO₃⁻ process, the addition of NaHCO₃ may give promising degradation efficiency of OTC. For a better visualized comparison, data on OTC degradation by UV/NaHCO₃ that has been published previously (Liu et al., 2015) and by UV/KNO₃ which has been shown in Fig. 1a are presented again in Fig. 2a. The synergistic effect in the presence of both KNO₃ and NaHCO₃ due to the generation and reaction of CO₃^{•-} was clearly shown.



The respective effect of different natural water constituents (e.g., inorganic anions, metal cations, and NOM) on the decomposition of OTC in UV/H₂O₂ and UV/PS AOPs has been extensively evaluated in our previous work (Liu et al., 2015, 2016a, 2016b). In this study, the OTC degradation by UV/H₂O₂ and UV/PS in the presence of both NaHCO₃ and other water constituents was investigated to assess the significance of CO₃^{•-} in these two AOPs (Eq. (9) and (10) (Buxton et al., 1988; Neta et al., 1988)). As shown in Fig. 2b and c, the addition of NaHCO₃ showed a promoting effect in all studied

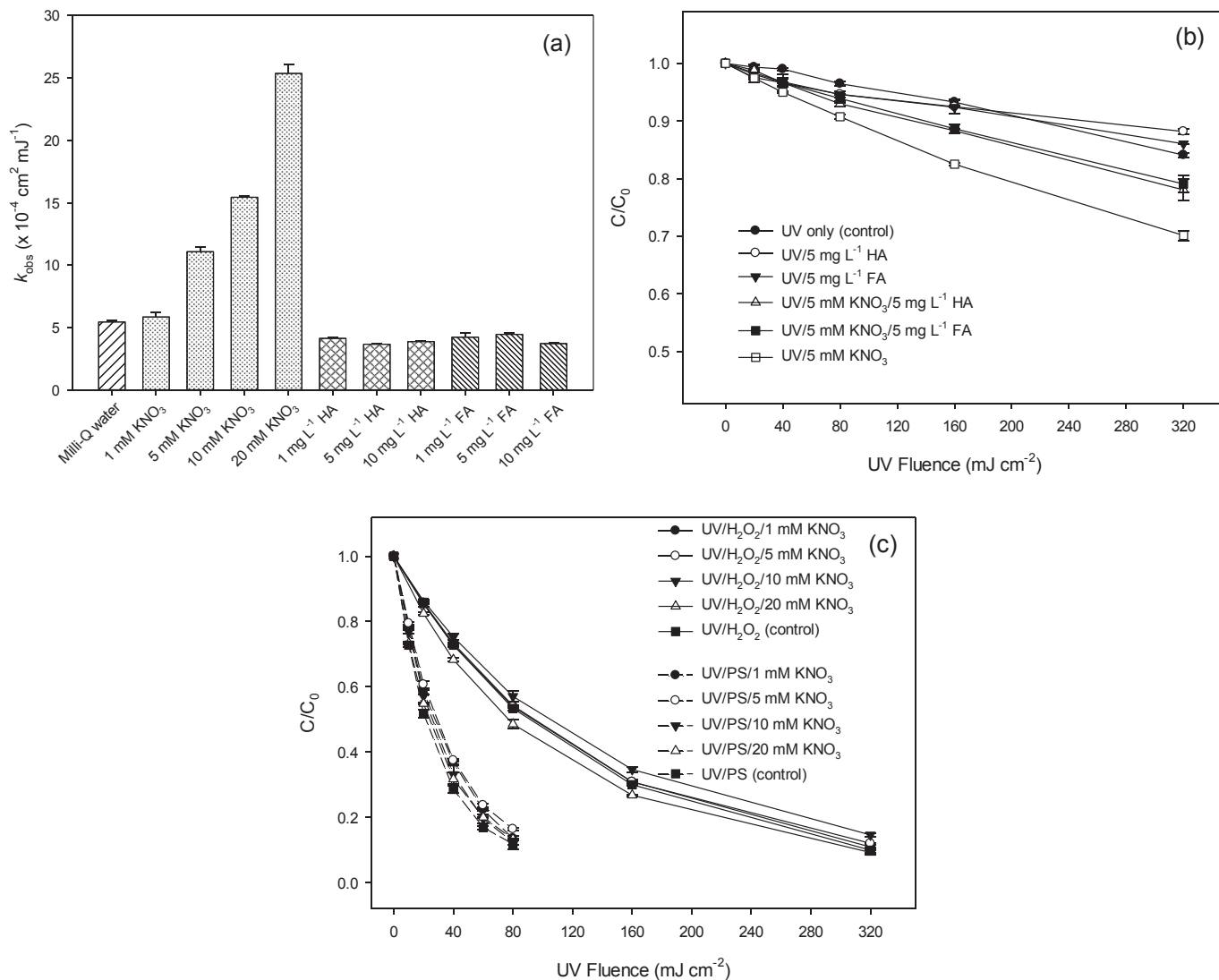
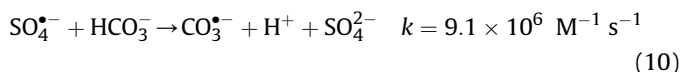


Fig. 1. (a) Influence of NO_3^- and NOM on OTC degradation by UV only. (b) Degradation of OTC by UV only with the addition of KNO_3 and HA or FA. (c) Degradation of OTC by UV/ H_2O_2 or UV/PS in the presence of various concentrations of KNO_3 . $[\text{OTC}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = [\text{PS}]_0 = 1 \text{ mM}$, no phosphate buffer. All the experiments were conducted in Milli-Q water (pH = 5.8).

reaction conditions indicating the importance of $\text{CO}_3^{\bullet-}$. This was a beneficial finding especially when bicarbonate is commonly present in natural waters.



3.3. Degradation of OTC in natural water matrices

Natural water samples from lakes, a river and different treatment stages of a drinking water treatment plant were utilized as reaction matrices and spiked with $10 \mu\text{M}$ OTC. As described in Fig. 3, the different degradation efficiencies with UV/PS > UV/ H_2O_2 > UV only for OTC removal in various natural waters were observed, which was consistent with the effect of radical reactions, the lower bond energy of peroxide bond (O–O) in PS ($140.0 \text{ kJ mol}^{-1}$ (Yang et al., 2010)) than in H_2O_2 ($213.3 \text{ kJ mol}^{-1}$ (Yang et al., 2010)), and therefore higher radical quantum yield in UV/PS (Mark et al., 1990).

Though $\text{CO}_3^{\bullet-}$ has a significant role on the destruction of OTC, it can hardly be generated by UV/ CO_3^{2-} or UV/ HCO_3^- (Liu et al., 2015). The presence of NOM might influence the photolysis efficiency of OTC, as discussed in Section 3.1. In this study, it resulted in a slight decrease in k_{obs} in these natural water samples by UV only compared with that in Milli-Q water. According to the pH of the water samples (Table 1), HCO_3^- was the main existing form of alkalinity. The presence of HCO_3^- could induce an enhanced effect (Fig. 2b), while the presence of NOM significantly inhibited the OTC degradation, as discussed above (Fig. 1b) and in our previous study (Liu et al., 2016b). Therefore, the removal of OTC was inhibited in all cases by UV/ H_2O_2 (Fig. 3). However, for UV/PS, even when TOC was as high as 94.68 mg L^{-1} , a comparable or even promoting effect was observed, which could be due to (1) less significant influence of $\text{SO}_4^{\bullet-}$ by NOM ($k > 6 \times 10^6 \text{ L (mol C)}^{-1} \text{ s}^{-1}$ (Gara et al., 2008)) than that of HO^{\bullet} ($k = 2.23 \times 10^8 \text{ L (mol C)}^{-1} \text{ s}^{-1}$ (Westerhoff et al., 2007)); (2) higher radical quantum yield of PS ($\Phi = 1.8$ (oxygen saturated) (Mark et al., 1990)) than that of H_2O_2 ($\Phi = 1.0$ (Baxendale and Wilson, 1957)); and (3) slightly better formation of $\text{CO}_3^{\bullet-}$ by $\text{SO}_4^{\bullet-}$ than by HO^{\bullet} as shown in Eqs. (9) and (10) (Buxton et al., 1988;

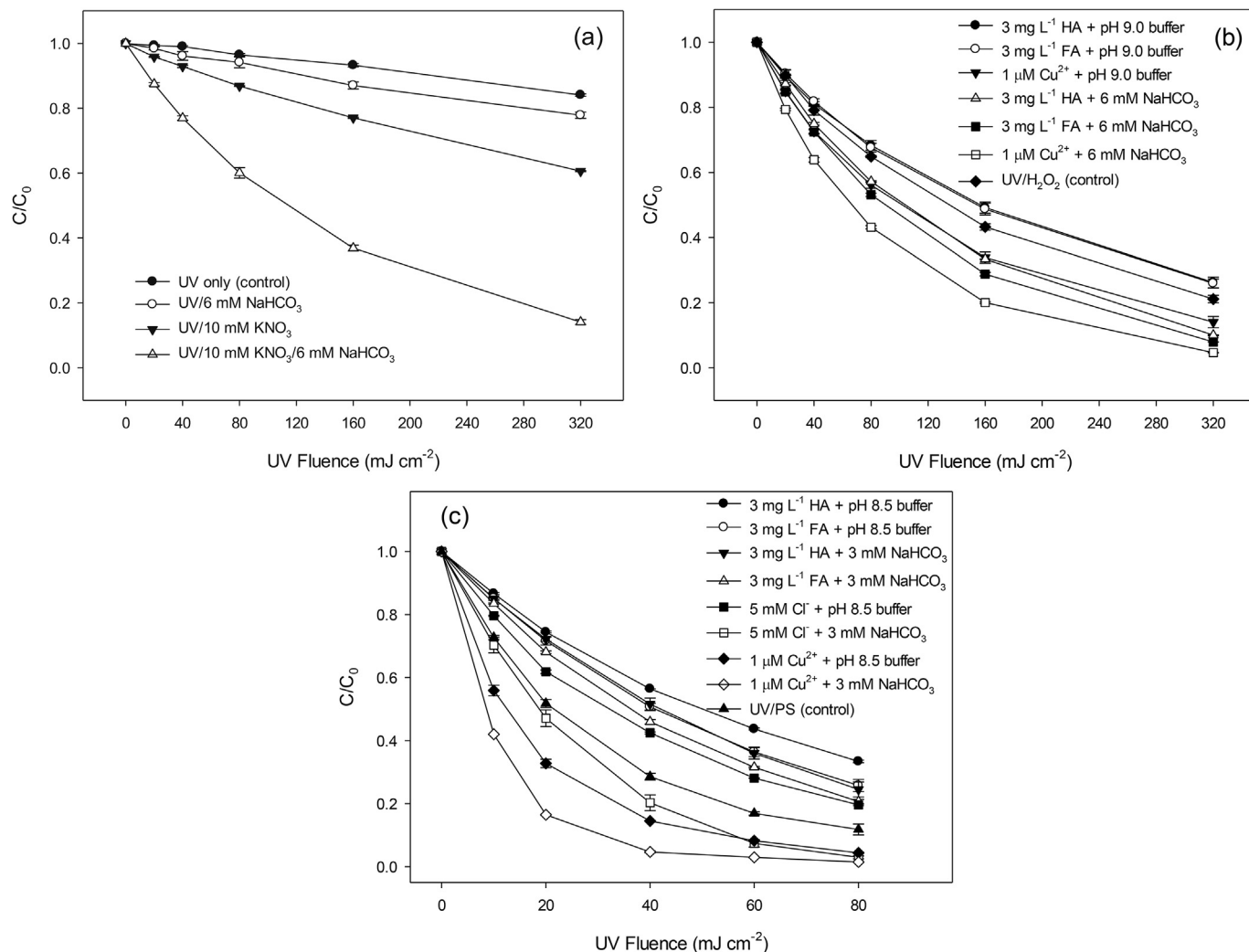


Fig. 2. Degradation of OTC at different conditions by (a) UV only, (b) UV/H₂O₂ and (c) UV/PS. [OTC]₀ = 10 μM, [H₂O₂]₀ = 0.5 mM, [PS]₀ = 1 mM, [KNO₃]₀ = 10 mM, [HA]₀ = [FA]₀ = 3 mg L⁻¹ (quantified by dissolved organic carbon, DOC), [Cu²⁺]₀ = 1 μM, [Cl⁻]₀ = 5 mM, [NaHCO₃]₀ = 6 mM for (a) and (b); 3 mM for (c), 50 mM phosphate buffer. With the addition of 6 mM and 3 mM NaHCO₃, the pH of reaction solutions was 9.0 and 8.5, respectively.

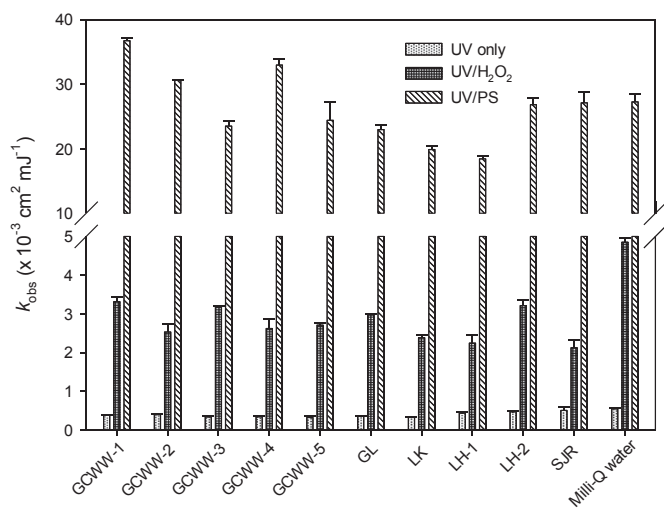


Fig. 3. Degradation of OTC in natural waters by UV only, UV/H₂O₂ and UV/PS. [OTC]₀ = 10 μM, [H₂O₂]₀ = 0.5 mM, [PS]₀ = 1 mM, no phosphate buffer. The pH of natural waters was in the range of 7.2–8.6.

Neta et al., 1988). The decrease of k_{obs} in natural waters than in Milli-Q water was reported by He et al. (2013, 2014) in the degradation of cylindrospermopsin (CYN) by UV/PS when the second-order rate constant of $\text{CO}_3^{\bullet-}$ with CYN was $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Zhang et al., 2015a), indicating that the higher rate constant of $\text{CO}_3^{\bullet-}$ with OTC ($k_{\text{CO}_3^{\bullet-}/\text{OTC}} = 2.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Liu et al., 2015)) was also an important factor for the observed effect of UV/PS in this study. These results suggested that UV/PS is a strongly advantageous treatment technology in degrading OTC and potentially other $\text{CO}_3^{\bullet-}$ sensitive organic contaminants in natural waters.

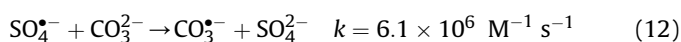
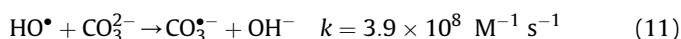
With the importance of $\text{CO}_3^{\bullet-}$ on the kinetic degradation of OTC being demonstrated again in this study, a further mechanism investigation into the transformation of OTC by $\text{CO}_3^{\bullet-}$ was carried out and is presented in the following section.

3.4. Degradation mechanism by carbonate radical

3.4.1. Degradation kinetics of OTC and byproducts

Though most of the previous experimental work was conducted using NaHCO₃, in this part of study, to generate a more significant amount of $\text{CO}_3^{\bullet-}$ for the transformation of OTC, Na₂CO₃ was used directly. The tert-butanol (t-BuOH), $k_{\text{HO}^\bullet/\text{t-BuOH}} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

(Buxton et al., 1988), $k_{\text{CO}_3^{\cdot-}/\text{t-BuOH}} < 1.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (Chen et al., 1973)) was added to UV/H₂O₂/Na₂CO₃ system to inhibit the reaction between OTC and HO[•]. As a control, the transformation of OTC in UV/Na₂CO₃ (pH = 10.4) and UV/pH 10.4 buffer (Milli-Q water controlled by 50 mM phosphate buffer with pH = 10.4) was also conducted. Besides, the byproduct detection and identification in UV/PS/t-BuOH/Na₂CO₃ were also included. The degradation kinetics of OTC (i.e., the parent compound) by these four reaction systems (all at the same pH) are shown in Fig. 4. The comparable degradation by UV/Na₂CO₃ and UV/pH 10.4 buffer indicated apparently the negligible effect of CO₃^{•-} in UV/Na₂CO₃ system for removing OTC. The increased OTC degradation by UV/H₂O₂/t-BuOH/Na₂CO₃ and UV/PS/t-BuOH/Na₂CO₃ than by UV/Na₂CO₃ or UV/pH 10.4 buffer was therefore attributed to CO₃^{•-} reaction. Though SO₄^{•-} has a much lower rate constant with CO₃^{•-} than HO[•], as shown in Eqs. (11) and (12) (Buxton et al., 1988; Zhang et al., 2015b), with the higher radical quantum yield of PS and the less SO₄^{•-} scavenging effect from t-BuOH ($k_{\text{SO}_4^{\cdot-}/\text{t-BuOH}} = 8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Clifton and Huie, 1989)), the lower initial PS concentration of 0.2 mM in UV/PS/t-BuOH/Na₂CO₃ was found to have comparable removal of OTC with 0.5 mM H₂O₂ in UV/H₂O₂/t-BuOH/Na₂CO₃.



The detected reaction byproducts with mass to charge ratio (m/z), retention time (RT) and formula in the above four systems are presented in Table S1 in SI. Their relative formation and evolution are shown in Fig. 5a–d. It should be noted, however, that in this case, the volume obtained from the MassHunter data analysis software was applied directly as a reference because of the lack of standards. Different signal strength (i.e., absolute volume numbers in y-axis) in different systems might be due to the influence of high concentrations of carbonate, phosphate buffer and/or t-BuOH on the LC-QTOF/MS analysis. It is clearly shown in Figs. 4 and 5 that UV only at high pH and CO₃^{•-} could degrade not only OTC but also its byproducts. The same byproducts speciation probably indicated a similar OTC transformation mechanism in these systems. The significant relative formation of m/z 431 and 475 distinguished their

reaction mechanism from UV only at near neutral pH and HO[•]/SO₄^{•-} reactions where m/z 415 was the major relatively byproduct (Liu et al., 2016a, 2016b). Regardless of how CO₃^{•-} was generated in UV/H₂O₂/t-BuOH/Na₂CO₃ or UV/PS/t-BuOH/Na₂CO₃ (Figs. 4, 5a and 5b), the mechanism as indicated by the formed byproducts seemed to be the same, suggesting the potential implication of current research outcome in other CO₃^{•-} based processes.

3.4.2. Potential degradation mechanism in the two control systems, i.e., UV/Na₂CO₃ and UV/pH 10.4 buffer

Compared to the degradation and transformation of OTC in UV/Milli-Q water without any pH control (Liu et al., 2016b), there are two significant observations, i.e., (1) the significantly faster degradation of OTC by UV/Na₂CO₃ and UV/pH 10.4 buffer as shown in Fig. 4, and (2) much more byproducts being detected in these two systems as presented in Table S1. This indicated that certain unrecognized mechanism was probably involved on the transformation of OTC at high pH under UV-254 nm irradiation. Currently there is no such information available in the literature. More studies are still needed to fully elucidate the mechanism beneath. Preliminarily, excited state OTC* (as shown in Eq. (13)) was proposed to be responsible for the transformation of OTC under such conditions.



It is well-known that after UV irradiation including solar UV, NOM can be excited to NOM* which can further transfer an electron to other molecules to form other ROS, e.g., ¹O₂, O₂^{•-}, and HO[•] (Carlos et al., 2012; Cooper et al., 1989; Yu et al., 2010). The responsible structures for such excitation include phenolic, carbonyl and quinoid groups (Choudhry, 1981a, 1981b). The presence of tri-carbonyl system and phenolic diketone moiety in the structure of OTC may indicate a similar transformation pathway via the excitation of OTC to OTC*. This can be further supported by previous studies showing that at higher pH, there is a red-shift in the absorption spectrum of OTC with a higher molar absorptivity being reported at 254 nm (Liu et al., 2015; Zhao et al., 2013). After excitation, the reactive radicals could be generated, as presented in Eqs. (14)–(16) (Garg et al., 2011; He et al., 2015; Zhang et al., 2012). Besides, ¹O₂ was reported to be generated more readily under simulated solar light irradiated OTC in the basic pH conditions (Zhao et al., 2013), which might also participate in the destruction of OTC. With comparable degradation kinetics of both parent OTC and byproducts for UV/Na₂CO₃ and UV/pH 10.4 buffer, it is logical to assume that excited OTC* is a key element for the transformation of OTC at the elevated pH condition. Similar to NOM*, after the transfer of an electron to other molecules, the subsequent reactions could be similar to those with reactive radicals via electron transfer and/or hydrogen abstraction such as those discussed below on CO₃^{•-} reaction mechanism. The potential pathways could therefore be elucidated. For example, Lipczynska-Kochany and Bolton (1992) have reported that *p*-benzoquinone, hydroquinone and 2-hydroxy-*p*-benzoquinone were the main byproducts in the direct photolysis of phenol. The m/z 477, 475 and 491 in this study could be produced similarly by direct photolysis. Again, as mentioned above, in this study, there was a lack of tools necessary to confirm the role of OTC*, and therefore no more discussion on the OTC transformation mechanism at high pH under UV irradiation is provided herein.

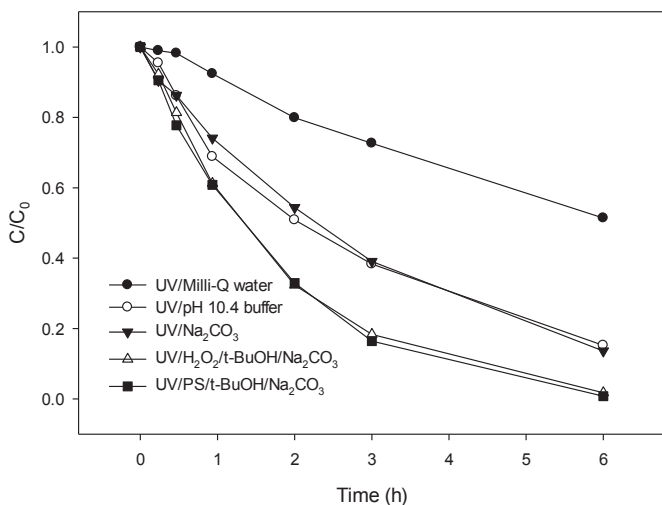


Fig. 4. Destruction of OTC in different reaction systems. [OTC]₀ = 40 μM, [H₂O₂]₀ = 0.5 mM, [PS]₀ = 0.2 mM, [Na₂CO₃]₀ = 3 mM, [t-BuOH]₀ = 10 mM, 50 mM phosphate buffer. With the addition of 3 mM Na₂CO₃, the pH of reaction solutions was 10.4. The OTC degradation by UV/Milli-Q water has been published in our previous work (Liu et al., 2016b).

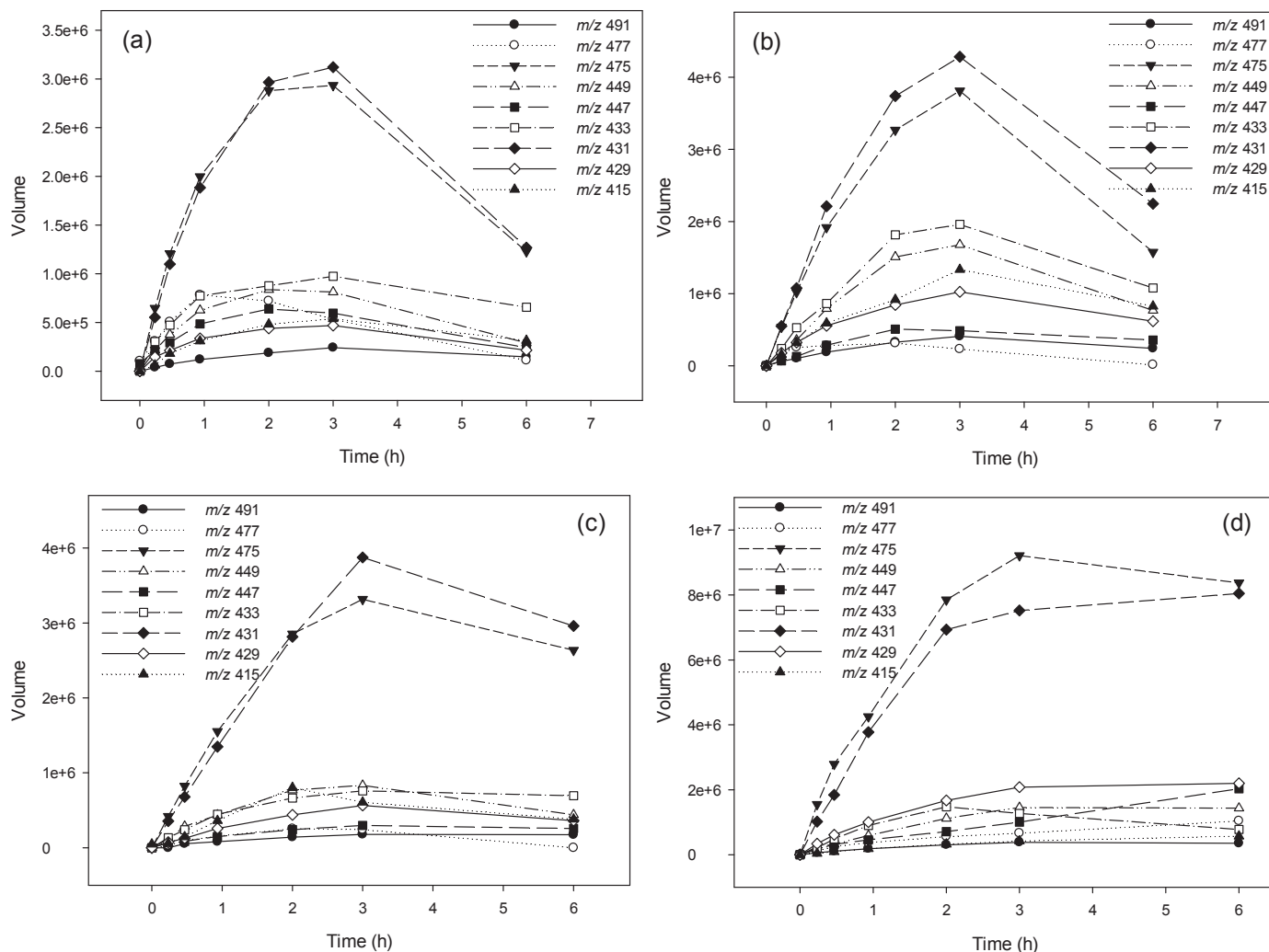


Fig. 5. Evolution of the main degradation byproducts by (a) UV/H₂O₂/t-BuOH/Na₂CO₃, (b) UV/PS/t-BuOH/Na₂CO₃, (c) UV/Na₂CO₃ and (d) UV/pH 10.4 buffer. [OTC]₀ = 40 μM, [H₂O₂]₀ = 0.5 mM, [PS]₀ = 0.2 mM, [Na₂CO₃]₀ = 3 mM, [t-BuOH]₀ = 10 mM, 50 mM phosphate buffer. With the addition of 3 mM Na₂CO₃, the pH of reaction solutions was 10.4.

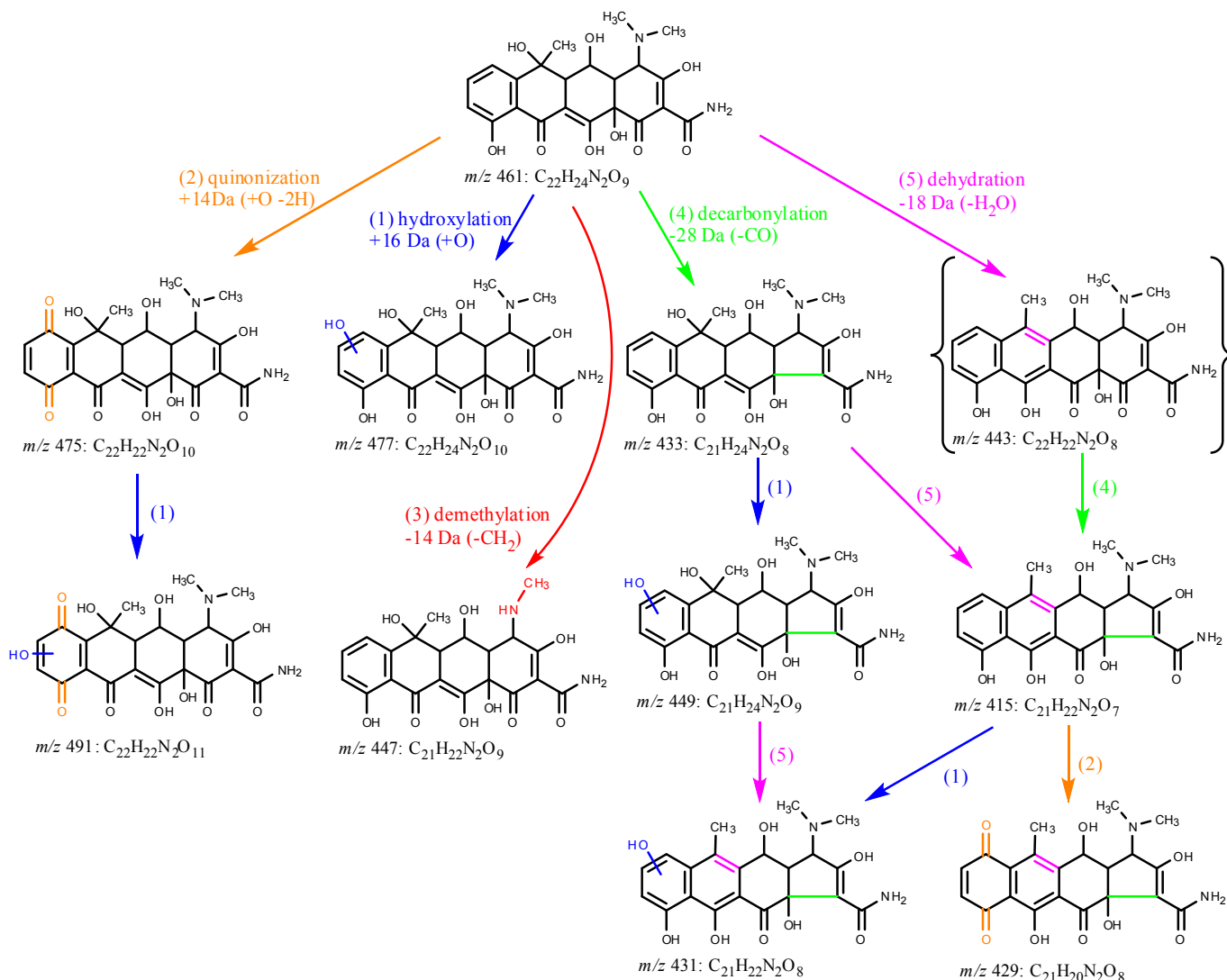


3.4.3. Proposed OTC transformation mechanism by carbonate radical

The speciation of the detected byproducts was the same in the four evaluated reaction systems. However, the apparent faster formation and further degradation of the byproducts probably indicated the involvement of CO₃^{•-} in UV/H₂O₂/t-BuOH/Na₂CO₃ and UV/PS/t-BuOH/Na₂CO₃ systems. In addition to the mass spectrum analysis of OTC (Liu et al., 2016b) and certain byproducts (Figs. S2–S5 in SI), photochemistry and radical chemistry theories were also applied in the structural assignment. The potential OTC transformation mechanism by CO₃^{•-} in UV/H₂O₂/t-BuOH/Na₂CO₃ or UV/PS/t-BuOH/Na₂CO₃ system was therefore proposed, exhibiting five different reaction pathways including hydroxylation (+16 Da), quinonization (+14 Da), demethylation (−14 Da), decarbonylation (−28 Da) and dehydration (−18 Da), as depicted in Scheme 1.

- (1) Hydroxylation and quinonization (pathways 1 and 2 in Scheme 1, respectively) were two important reaction paths. The excited OTC*, especially at the tricarbonyl system and phenolic

diketone moiety as indicated above, might also be generated in UV/H₂O₂/t-BuOH/Na₂CO₃ and UV/PS/t-BuOH/Na₂CO₃ systems. Due to the electrophilic nature of CO₃^{•-}, the excited OTC* could probably transfer more easily an electron to CO₃^{•-}, contributing to the transformation of OTC in UV-based processes. For ground state OTC, phenol moiety (ring D) and dimethylammonium group at C4 (Fig. S6 in SI) are probably the most reactive sites for electrophilic CO₃^{•-} attack. The second-order rate constant of CO₃^{•-} with dimethylammonium group was estimated to be 10⁶ M⁻¹ s⁻¹ based on the rate constants of structurally similar compounds such as N,N-dimethyl-tert-butylamine ($k_{\text{CO}_3^\bullet-/(\text{CH}_3)_3\text{CN}(\text{CH}_3)_2} = 3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and N,N-dimethylbenzylamine ($k_{\text{CO}_3^\bullet-/C_6H_5CH_2N(\text{CH}_3)_2} = 3.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Elango et al., 1985). According to the group contribution theory (Minakata et al., 2009), phenol moiety might be attacked more readily by CO₃^{•-} due to its higher reactivity with CO₃^{•-} ($k_{\text{CO}_3^\bullet-/C_6H_5OH} = 2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Chen and Hoffman, 1973)). As described in detail in Scheme S1 in SI, through the transfer of an electron from phenol moiety to CO₃^{•-}, a radical cation could be formed (Canonica et al., 1995). It could then undergo proton transfer to produce a phenoxyl radical, which could exist in several canonical forms. For example, the *ortho*- and *para*-



Scheme 1. Proposed degradation mechanisms of OTC by carbonate radical: (1) hydroxylation, (2) quinonization, (3) demethylation, (4) decarbonylation and (5) dehydration. The byproduct with “{ }” was not detected in this work. [OTC]₀ = 40 μM, [H₂O₂]₀ = 0.5 mM, [PS]₀ = 0.2 mM, [Na₂CO₃]₀ = 3 mM, [t-BuOH]₀ = 10 mM, no phosphate buffer.

positions of phenoxy radical species have been shown to have high radical electron spin densities (Shimazaki, 2013). The followed attack by oxygen generated a peroxy radical and subsequently an alkoxy radical (Busset et al., 2007; Canonica et al., 1995). Hydroxylation byproduct *m/z* 477 and quinonization byproduct *m/z* 475 could then be formed by disproportionation (Mazellier et al., 2007), which was also supported by their mass spectrum analysis as shown in Figs. S2 and S3. The fragmentation from fragment ions *m/z* 424 to 381 and *m/z* 440 to 395 by losing imine and dimethylamine for *m/z* 477 and 475, respectively (Kamel et al., 2002), indicated the intact dimethylammonium group and therefore a reaction in ring D. For *m/z* 475, *p*-benzoquinone-OTC was shown in Scheme 1 due to the detection of only one signal, though *o*-benzoquinone-OTC could not be excluded. The results are in agreement with the reported formation of benzoquinone and dihydroxybenzenes during the reaction of phenol with CO₃^{•-} (Busset et al., 2007). The *m/z* 491 could then be formed from *m/z* 475 by a second hydroxylation (Scheme 1).

(2) Demethylation (pathway 3 in Scheme 1) referred to the removal of one methyl group from the dimethylammonium

group at C4 resulting in the generation of the byproduct *m/z* 447. Demethylation byproduct was also observed by Mazellier et al. (2007) in the degradation of fenuron using UV/[Co(NH₃)₅CO₃]⁺ where CO₃^{•-} can be generated. It was thus believed that the presence of CO₃^{•-} could be effective in removing the methyl group. The reaction probably started with H-abstraction at the activated methyl group. Following a similar O₂ attack, peroxy radical formation and subsequently C=N formation, a C=N bond cleavage (i.e., demethylated) byproduct could be formed (Liu et al., 2016b).

(3) Decarbonylation and dehydration (pathways 4 and 5 in Scheme 1, respectively) could occur under UV direct photolysis leading to the formation of *m/z* 433 and 415, which has been discussed extensively in our previous work (Liu et al., 2016b). Briefly, the enolic acetylaceton moiety in ring A (C12a-C4) underwent type I cleavage at C12a-C1 bond producing a diradical intermediate followed by the loss of CO to form the other diradical intermediate. The *m/z* 433 could then be generated from the latter diradical through the ring closure. Though *m/z* 443 (-18 Da) was not detected in this study, the dehydration pathway could still occur at C6-C5a resulting in

the formation of a stable aromatic ring at C based on the tautomerization of the C11-C12 keto/enol (Liu et al., 2016b). The formed m/z 433 could be hydroxylated to the m/z 449 which could also undergo dehydration reaction to generate m/z 431 (Scheme 1). The mass spectra of m/z 449 and 431 are presented in Figs. S4 and S5, supporting again our previous conclusion that decarbonylation occurred in ring A due to the absence of the fragment ions m/z 58, 98, 126 and 154 which are all resulted from ring A for OTC (Kamel et al., 2002; Liu et al., 2016b; Vartanian et al., 1998). The m/z 415 could be transformed to the m/z 431 and 429 by the hydroxylation and quinonization pathways, respectively.

4. Conclusions

This study explored the role of $\text{CO}_3^{\bullet-}$ in the degradation of OTC by UV only, UV/ H_2O_2 and UV/PS AOPs through kinetics evaluation and mechanism investigation. Presence of NOM slightly inhibited OTC degradation by UV direct photolysis; while an enhancement effect was observed in the presence of NO_3^- due to the generation of HO^\bullet , which was confirmed by the addition of a common HO^\bullet quenching agent. However, no significant influence of NO_3^- was observed in the UV/ H_2O_2 or UV/PS process. For UV only process in the presence of both NaHCO_3 and NO_3^- , $\text{CO}_3^{\bullet-}$ was found to play a positive role on the destruction of OTC. Such influence was also observed in the other two AOPs with NaHCO_3 and other natural water constituents such as NOM, Cu^{2+} , and Cl^- . When natural waters were used as reaction matrices, an inhibiting effect was observed for UV only and UV/ H_2O_2 ; while a comparable or even promoting effect was observed for UV/PS process where the generation of $\text{CO}_3^{\bullet-}$ could be significant. After elucidating the potential contribution of UV direct photolysis via excited state OTC* at an elevated reaction pH condition, potential OTC degradation mechanism by $\text{CO}_3^{\bullet-}$ was proposed showing five different transformation pathways including hydroxylation (+16 Da), quinonization (+14 Da), demethylation (-14 Da), decarbonylation (-28 Da), and dehydration (-18 Da). Additionally, the main byproducts from both systems, i.e., UV at high pH and $\text{CO}_3^{\bullet-}$ (generated either by UV/ H_2O_2 /t-BuOH/ Na_2CO_3 or by UV/PS/t-BuOH/ Na_2CO_3), have been shown to be different from those by UV at near neutral pH and $\text{HO}^\bullet/\text{SO}_4^{\bullet-}$ reactions (Liu et al., 2016a, 2016b). This study demonstrates again the important role of $\text{CO}_3^{\bullet-}$ on the degradation of OTC and provides valuable information for the removal of OTC and potentially other $\text{CO}_3^{\bullet-}$ reactive organic contaminants from the contaminated waters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.03.011>.

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