



Chlorination and bromination of olefins: Kinetic and mechanistic aspects

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ABSTRACT

Hypochlorous acid (HOCl) is typically assumed to be the primary reactive species in free available chlorine (FAC) solutions. Lately, it has been shown that less abundant chlorine species such as chlorine monoxide (Cl₂O) and chlorine (Cl₂) can also influence the kinetics of the abatement of certain organic compounds during chlorination. In this study, the chlorination as well as bromination kinetics and mechanisms of 12 olefins (including 3 aliphatic and 9 aromatic olefins) with different structures were explored. HOCl shows a low reactivity towards the selected olefins with species-specific second-order rate constants <1.0 M⁻¹s⁻¹, about 4–6 orders of magnitude lower than those of Cl₂O and Cl₂. HOCl is the dominant chlorine species during chlorination of olefins under typical drinking water conditions, while Cl₂O and Cl₂ are likely to play important roles at high FAC concentration near circum-neutral pH (for Cl₂O) or at high Cl⁻ concentration under acidic conditions (for Cl₂). Bromination of the 12 olefins suggests that HOBr and Br₂O are the major reactive species at pH 7.5 with species-specific second-order rate constants of Br₂O nearly 3–4 orders of magnitude higher than of HOBr (ranging from <0.01 to >10³ M⁻¹s⁻¹). The reactivities of chlorine and bromine species towards olefins follow the order of HOCl < HOBr < Br₂O < Cl₂O ≈ Cl₂. Generally, electron-donating groups (e.g., CH₂OH- and CH₃-) enhances the reactivities of olefins towards chlorine and bromine species by a factor of 3–10², while electron-withdrawing groups (e.g., Cl-, Br-, NO₂-, COOH-, CHO-, -COOR, and CN-) reduce the reactivities by a factor of 3–10⁴. A reasonable linear free energy relationship (LFER) between the species-specific second-order rate constants of Br₂O or Cl₂O reactions with aromatic olefins and their Hammett σ⁺ was established with a more negative ρ value for Br₂O than for Cl₂O, indicating that Br₂O is more sensitive to substitution effects. Chlorinated products including HOCl-adducts and decarboxylated Cl-adduct were identified during chlorination of cinnamic acid by high-performance liquid chromatography/high resolution mass spectrometry (HPLC/HRMS).

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1. Introduction

Chemical oxidants such as chlorine and ozone have been applied for water disinfection since the 20th century (Le Pauloué and Langlais, 1999; McGuire, 2006; von Sonntag and von Gunten, 2012). Consecutively, they have been used for the transformation/abatement of inorganic and/or organic micropollutants detected in water (von Gunten, 2018). However, undesirable dis-

infection by-products (DBPs) or harmful transformation products can be generated from the reactions of oxidants with water matrix components and micropollutants under certain conditions (Boorman, 1999; Gallard and von Gunten, 2002a, b; Richardson et al., 2007; Sedlak and von Gunten, 2011).

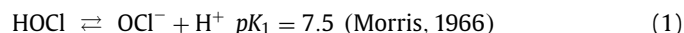
Chlorine. Free available chlorine (FAC, HOCl+OCl⁻) is the most used oxidant for drinking water disinfection globally, which can transform numerous inorganic and organic micropollutants (Deborde and von Gunten, 2008; Gray, 2014). FAC shows a fast reaction with many inorganic compounds (e.g., Fe(II), As(III), CN⁻, and NO₂⁻) under water treatment conditions, but not for others such as Mn(II) (Deborde and von Gunten, 2008; Allard et al., 2013). The reactivity of FAC towards organic compounds is

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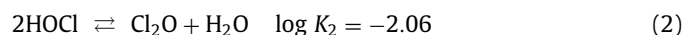
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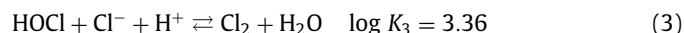
influenced by their electronic properties with species-specific second-order rate constants varying over a wide range from < 0.1 to $10^9 \text{ M}^{-1}\text{s}^{-1}$ (Deborde and von Gunten, 2008). In general, FAC is prone to reaction with compounds containing electron-rich sites including activated aromatic systems (Gallard et al., 2002b; Acero et al., 2005a; Criquet et al., 2015; Gao et al., 2018), neutral amines (Armesto et al., 1993; Antelo et al. 1995; Dodd and Huang, 2004; Dodd et al., 2005), and reduced sulfur moieties (Armesto et al., 2000; Pattison and Davies, 2001). Chlorine speciation is another factor influencing FAC reactivity towards organic compounds. HOCl and OCl^- (Eq. (1), (Morris, 1966)) are often regarded as the main chlorine species during chlorination with HOCl often controlling reaction kinetics (Deborde and von Gunten, 2008).



However, other chlorine species such as chlorine monoxide (Cl_2O) and chlorine (Cl_2) have drawn increasing scientific attention (Sivey et al., 2010; Sivey and Roberts, 2012; Cai et al., 2013, 2017; Lau et al., 2016, 2019; Rose et al., 2020). Cl_2O is formed via dehydration of 2 HOCl molecules (Eq. (2), 25 °C, 0.0 M ionic strength (Sivey et al., 2010)).

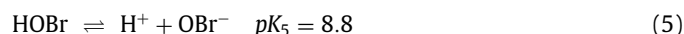
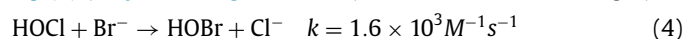


Furthermore, Cl_2 can be formed in FAC solutions containing chloride (Cl^-), especially at lower pH (Eq. (3), 25 °C, 0.0 M ionic strength (Sivey et al., 2010)).



These chlorine species are often overlooked due to their low concentrations, which are several orders of magnitude lower than HOCl/ OCl^- . For example, the concentrations of HOCl, OCl^- , Cl_2O , and Cl_2 are around 1.4×10^{-5} , 1.4×10^{-5} , 1.7×10^{-12} , and $2.3 \times 10^{-13} \text{ M}$, respectively, at pH 7.5 under typical drinking water chlorination conditions (e.g., [FAC] = 2.0 mg/L as $\text{Cl}_2 \approx 28 \mu\text{M}$, $[\text{Cl}^-] = 8 \text{ mg/L} \approx 0.23 \text{ mM}$, in this paper if not otherwise stated) (Text S1 and Figure S1a, supporting information (SI)). Yet, there is evidence that the low concentrations of Cl_2 and Cl_2O can be compensated by their high reactivities with some organic compounds (Sivey et al., 2010; Sivey and Roberts, 2012; Cai et al., 2013, 2017). For instance, Sivey et al. (2010) reported that the species-specific second-order rate constants for the reactions of HOCl, Cl_2O , and Cl_2 with dimethenamid were around 0.18, 1.37×10^6 , and $1.21 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, respectively, and Cl_2O contributed ~50% to the total FAC reactivity under typical drinking water chlorination conditions. Cai et al. (2013) showed that the contribution of Cl_2 to the transformation of antipyrine (an anti-inflammatory drug) by chlorine increased with decreasing pH with a contribution of >42% at pH <3.2, while Cl_2O had a relatively stable contribution (~23%) over the pH range of 4.0–7.0. Generally, Cl_2 can affect FAC reactivity towards some organic compounds at pH <7.5 in the presence of high concentration of Cl^- , while Cl_2O plays an important role around neutral pH for high FAC concentrations (Sivey et al., 2010; Sivey and Roberts, 2012; Cai et al., 2013; Lau et al., 2016).

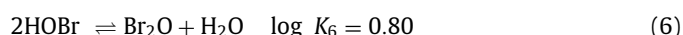
Bromine. Bromide (Br^-) is one of the key constituents of water matrixes and is highly relevant in oxidation processes (Heeb et al., 2014; Winid, 2015; Soltermann et al., 2016). Chlorination of Br^- -containing waters forms hypobromous acid (HOBr) and hypobromite (OBr^-) (Eq. (4) (Kumar and Margerum, 1987) and Eq. (5) (Troy and Margerum, 1991), 25 °C, 0.0 M ionic strength).



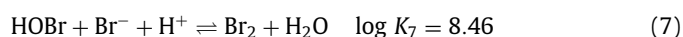
HOBr shows significant reactivities towards phenols, neutral amines, sulfamides, and sulfur-containing compounds with

reactivity generally higher than HOCl under similar condition (Gallard et al., 2003; Westerhoff et al., 2004; Heeb et al., 2014, 2017). For instance, Heeb et al. (2014) reported that the apparent second-order rate constants (k_{app}) of HOBr reactions with substituted phenols at pH 7.0 ($k_{\text{app}} \approx 10^3\text{--}10^5 \text{ M}^{-1}\text{s}^{-1}$) are on average about 3000 times higher than for HOCl. The presence of Br^- during chlorination can not only accelerate the transformation of micropollutants but also change the types and concentrations of DBPs formed from dissolved organic matter (Lee and von Gunten, 2009; Zhao et al., 2010; Zhai and Zhang, 2011; Ding et al., 2013; Liu et al., 2013; Liu et al., 2018).

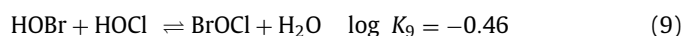
Similar to the case of FAC, Br_2O can be formed via dehydration of 2 HOBr molecules (Eq. (6), 25 °C, 0.0 M ionic strength (Sivey et al., 2013)).



Br_2 is formed in the presence of excess Br^- under acidic conditions (i.e., $[\text{Br}^-] > [\text{FAC}]$, Eq. (7), 25 °C, 0.0 M ionic strength (Beckwith et al., 1996)). However, such conditions are unlikely for most drinking waters.



Other mixed bromine-chlorine species such as BrCl and BrOCl can also be formed during chlorination of Br^- -containing waters (eqs. 8–9, 25 °C, 0.0 M ionic strength (Beckwith et al., 1996; Rose et al., 2020))



HOBr controls the speciation of bromine at pH 7.5 for typical drinking water conditions (i.e., [FAC] = 2.0 mg/L as $\text{Cl}_2 \approx 28 \mu\text{M}$, $[\text{Cl}^-] = 8 \text{ mg/L} \approx 0.23 \text{ mM}$, $[\text{Br}^-] = 100 \mu\text{g/L} \approx 1.25 \mu\text{M}$) with a concentration nearly 5–8 orders of magnitude higher than Br_2O , BrOCl , and BrCl (Text S2 and Figure S2a, SI). Br_2 may play an important role if excess Br^- ($[\text{Br}^-]_{\text{ex}}$) is present (e.g., [FAC] = 2.0 mg/L as $\text{Cl}_2 \approx 28 \mu\text{M}$, $[\text{Cl}^-] = 8 \text{ mg/L} \approx 0.23 \text{ mM}$, $[\text{Br}^-]_{\text{total}} = 2.3 \text{ mg/L} \approx 29.25 \mu\text{M}$, $[\text{Br}^-]_{\text{ex}} = [\text{Br}^-]_{\text{total}} - [\text{FAC}] = 1.25 \mu\text{M} \approx 100 \mu\text{g/L}$) with its concentration 5 orders of magnitude lower than concentration of HOBr at pH 7.5 (Text S2 and Figure S2b, SI). Recent studies demonstrated that these less abundant bromine species were inherently more reactive than HOBr, and they could influence bromination rates under typical drinking water conditions (Sivey et al., 2013, 2015). For instance, Sivey et al. (2013) showed that the species-specific second-order rate constants for the reactions of Br_2O , Br_2 , BrCl , and BrOCl with dimethenamid were up to $10^3\text{--}10^6$ times higher than for HOBr. BrCl is predominant at pH $< \approx 7.0$, while HOBr dominated the overall transformation of dimethenamid at pH $> \approx 7.0$ under typical drinking water chlorination conditions (i.e., [FAC] = 2.0 mg/L as $\text{Cl}_2 \approx 28 \mu\text{M}$, $[\text{Cl}^-] = 10.5 \text{ mg/L} \approx 0.3 \text{ mM}$, $[\text{Br}^-] = 100 \mu\text{g/L} \approx 1.25 \mu\text{M}$). Contributions of Br_2O , BrOCl , and BrCl were <20% in the pH range of 5–9. However, they become increasingly important at higher Cl^- (for BrCl), FAC (for BrOCl), or Br^- (leading to higher HOBr and consequently higher Br_2O concentrations) concentrations. For example, Br_2O contributed ~3.5% to dimethenamid transformation under typical drinking water chlorination conditions at pH 7.5 in the presence of 1.25 μM Br^- ($\approx 100 \mu\text{g/L}$), while it contributed ~13.1% and 28.4% when the Br^- concentration increased to 5.0 μM ($\approx 400 \mu\text{g/L}$) and 10 μM Br^- ($\approx 800 \mu\text{g/L}$), respectively, under similar conditions (Sivey et al., 2013).

Overall, the available kinetic data suggest that the less abundant chlorine or bromine species (e.g., Cl_2O , Cl_2 , Br_2O , Br_2 , BrCl , and BrOCl) can play significant roles in the chlorination or bromination of various organic compounds such as *p*-xylene (Voudrias and Reinhard, 1988a, Voudrias and Reinhard, 1988b), ethers (Sivey and

Roberts., 2012; Sivey et al., 2015), antipyrine (Cai et al., 2013), aminopyrine (Cai et al., 2017), (chloro)-phenols (Lau et al., 2016), and dimethenamid (Sivey et al., 2010, 2013), especially those reacting with relatively low second-order rate constants with HOCl and HOBr.

Olefinic compounds. Olefins are electron-rich compounds, which are frequently present in anthropogenic and natural micropollutants such as carbamazepine, ionones, β -cyclocitral, and microcystins (Tixier et al., 2003; Nikolaou et al., 2007; Peter et al., 2009; Chen et al., 2010). Limited studies show that HOCl has a low to negligible reactivities towards olefins (Prütz, 1998; Pattison et al., 2003; Acero et al., 2005b; Rodriguez et al., 2008; Zhang et al., 2012), while bromine has moderate to high reactivities, however, generally only limited kinetic information is available (Staff et al., 2007, 2008). It has been reported that the relative importance of Cl_2O and Cl_2 increases with decreasing reactivity of the target compound towards HOCl (Sivey et al., 2012). Recently, Lau et al. (2019) reported that Cl_2 and Cl_2O dominated the chlorination kinetics of cyclic olefins (e.g., β -ionone) at high Cl^- and HOCl concentrations, respectively. Even though these studies provide some insights into the reactivity of FAC and bromine (including their speciation) towards selected olefin structures, there is still a significant knowledge gap in this field.

The aim of this study was to establish kinetic and mechanistic data on chlorine or bromine reactions with olefins with various substituents. Both aliphatic and aromatic olefins were investigated in this study. The effect of FAC and bromine speciation on the apparent second-order rate constants was investigated by pH variations and/or concentration variations of FAC and bromine. Based on these systematic variations of the reaction conditions, species-specific second-order rate constants for various chlorine (mainly HOCl, Cl_2O , and Cl_2) and bromine species (mainly HOBr and Br_2O) were determined to assess their importance during chlorination or bromination of various olefinic compounds. Furthermore, products from the chlorination of cinnamic acid were identified.

2. Materials and methods

2.1. Chemicals and reagents

The 12 selected olefins (Fig. 1) were purchased from Sigma Aldrich and used without further purification (Table S1 (SI) for more information on purities and CAS numbers). Stock solutions of the olefins (4 mM) were prepared by dissolving the compounds in methanol due to their low solubility in water. Spiking solutions of olefins were prepared by diluting the methanolic stock solutions to 1 mM by ultrapurified water (18.2 $\Omega\text{M}/\text{cm}$) obtained from a Millipore Milli-Q water purification system. The final concentrations of methanol introduced in the reaction solutions were <2.5% (v/v), which was demonstrated in control experiments to have a negligible effect on the FAC and bromine concentrations for the relevant time scales in this study. FAC stock solutions (~45.0 mM) were obtained by diluting a commercial sodium hypochlorite (NaOCl) solution (Sigma Aldrich, reactive chlorine 10–15%) and quantified spectrophotometrically by measuring the OCl^- absorbance at 292 nm ($\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$) (Kumar and Margerum, 1987) every week (concentration changed $\leq 5.0\%$ within one week).

Stock solutions of bromine were obtained by oxidation of potassium bromide (KBr) solutions with a 1.2 times higher ozone concentration (1.0–1.1 mM) at pH 4.0 in 2 mM phosphate buffer to guarantee full oxidation of bromide (Pinkernell et al., 2000). After 24 h, the HOBr solution was purged with nitrogen for 15 min to remove residual ozone and then the solution pH was elevated to 12.0 using NaOH to avoid the disproportionation of HOBr (Beckwith and Margerum, 1997). The HOBr stock solution (0.8–0.9 mM) was stored at 4 °C in brown bottles and standard-

ized spectrophotometrically by measuring the OBr^- absorbance at 329 nm ($\epsilon = 332 \text{ M}^{-1} \text{ cm}^{-1}$) at pH 12 before use (Kumar and Margerum, 1987). Fresh HOBr solutions were prepared every week.

2.2. Kinetic experiments

All experiments were performed in duplicates at room temperature (23 ± 2 °C) either using amber glass vials with PTFE caps or by stopped-flow. For slow reactions, to apply pseudo first-order conditions, excess FAC or bromine ($[\text{FAC}]_0/[\text{olefin}]_0$ or $[\text{bromine}]_0/[\text{olefin}]_0 \geq 10$) working solutions were introduced into pH buffered solutions (10 mM acetic acid for pH 5.0–6.5, 10 mM phosphate buffer for pH 7.0 and 7.5, and 10 mM borate for pH 8.0–9.0). Particularly, in experiments investigating the impacts of Cl^- on the chlorination kinetics of CA and Dien-COOH (Fig. 1), KCl (0–20 mM) was also added to acetic acid (10 mM) buffered solutions at pH 5.0. Thereafter, the solution pH was measured and re-adjusted (addition of FAC or bromine slightly increased the pH) by H_2SO_4 (1 M) or NaOH (1 M) to maintain the reaction solution at the desired pH. Finally, a selected olefin (3–5 μM) was added to the vigorously stirred solution to initiate the reaction and the vials were immediately capped. 1 mL samples were withdrawn after pre-determined reaction times and quenched with thiosulfate ($[\text{thiosulfate}]/[\text{FAC}]_0$ or $[\text{thiosulfate}]/[\text{bromine}]_0 = 5$) for high-performance liquid chromatography (HPLC) analysis of the olefins. Control experiments showed that thiosulfate had a negligible impact on the stability of the chlorinated and brominated samples. The pH changed by ≤ 0.1 unit over the course of all the reactions.

For the fast reactions of bromine with Dien-COOH and Dien-OH (Fig. 1), a stopped-flow system (Hi-Tech Scientific SF-61DX2) was used. The change in absorbance of Dien-COOH ($\lambda = 255$ nm) and Dien-OH ($\lambda = 228$ nm) was monitored at pH 7.5 (10 mM phosphate buffer) under pseudo-first order conditions with excess bromine ($[\text{bromine}]_0/[\text{Dien-COOH}]$ or $[\text{bromine}]_0/[\text{Dien-OH}]_0 > 10$). The kinetic data was analyzed by the software Kinetic Studio 2.x, TgK Scientific (Shin et al., 2020).

2.3. Analyses of olefins, oxidants, and transformation products

A Thermo Scientific HPLC (UltiMate 3000) equipped with a Symmetry C18 column (125 \times 3.0 mm, 5 μm particle size) and a Diode Array Detector (UltiMate 3000) was used for the determination of the selected olefins. The isocratic mobile phase consisted of acetonitrile (phase A) and 10 mM phosphoric acid (pH ~2.3, phase B) at a flow rate of 0.8 mL/min (SI, Table S1 and Figure S3 for more information). UV-vis spectra were measured by a Shimadzu UV-1800 spectrophotometer. The initial and final concentrations of FAC and bromine in working solutions were measured by the ABTS method (Pinkernell et al., 2000), and the results indicated that the oxidant concentrations varied <10% for all the kinetic runs. The Cl^- concentration in the FAC solution was analyzed by ion chromatography (IC) (ICS3000, Thermo Scientific) with a limit of quantification (LOQ) of 0.05 mg/L.

For the identification of transformation products of CA (Fig. 1) by FAC, samples were measured by a Thermo Fisher Scientific Q Exactive Plus high-resolution mass spectrometer (HRMS) coupled to a Dionex UltiMate 3000 LC Pump and a Thermo Pal autosampler. An Atlantis® T3 C18 column (3.0 \times 150 mm, 3 μm particle size) was used for separation. The mobile phase consisted of water and methanol with both of them containing 1% formic acid at a flow rate of 0.3 mL/min. An initial MS full-scan (mass resolution 140000 at 200 Da) followed by five data-dependent fragmentation MS/MS experiments (mass resolution 17500 at m/z 200) were performed in both positive and negative electrospray ionization mode (i.e., ESI(+) and ESI(-)).

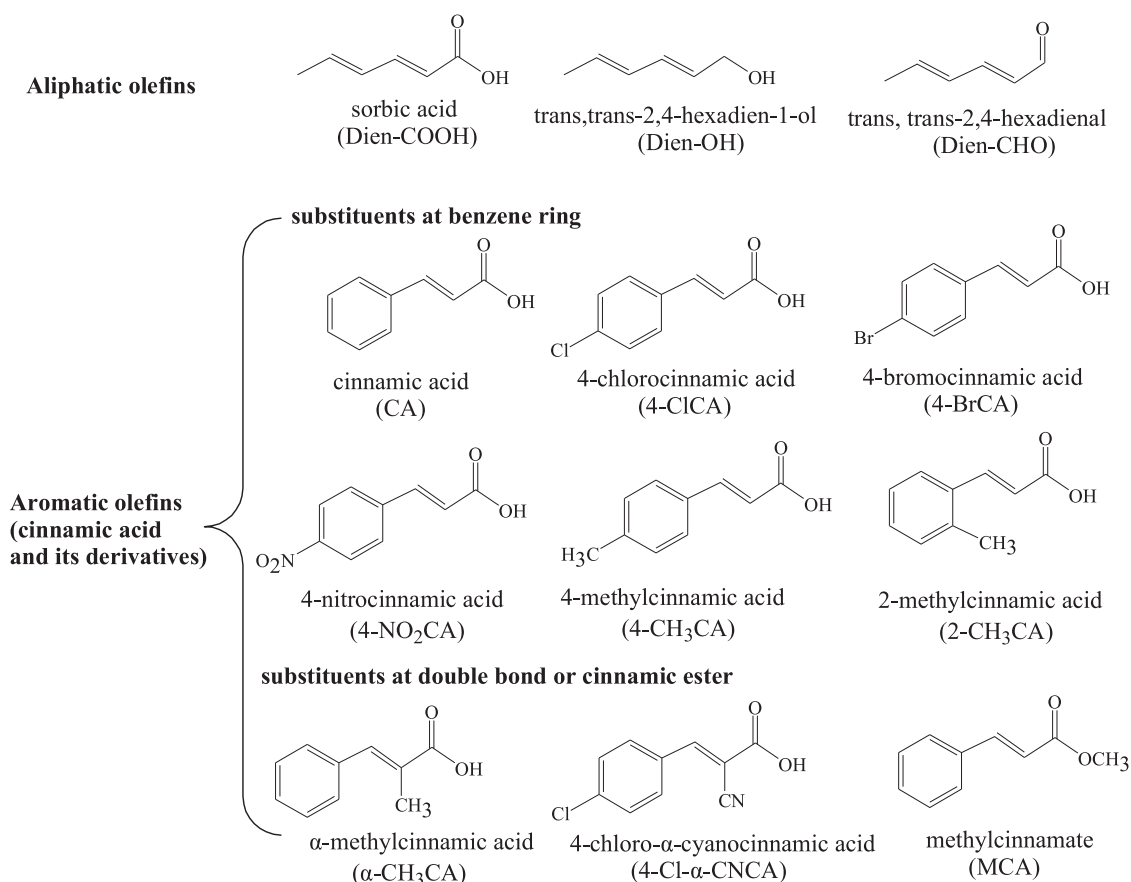


Fig. 1. Chemical structures of the selected aliphatic and aromatic olefins.

2.4. Data modeling

Pseudo-first-order rate constants (k_{obs}) for the reactions of olefins with FAC or bromine were determined from linear regressions of the experimental $\ln[\text{olefins}]_t/[\text{olefins}]_0$ vs time data. Second-order rate constants (k_{app}) for the reactions of chlorine species (HOCl, Cl₂O, and Cl₂) and bromine species (HOBr and Br₂O) with olefins were calculated by nonlinear least-squares regressions in Origin 8.5 (Seifert, 2014).

3. Results and discussion

3.1. Chlorination of olefins

3.1.1. Kinetics of FAC reactions with olefins

Figure S4 (SI) shows the first-order plots for the oxidation of olefins (5.0 μM) by FAC (0.5–4.5 mM) at pH 7.5. The good linear correlations suggest that the reactions are first-order with respect to olefins. The reaction rates for chlorination of olefins in the presence of excess FAC can be described by Eqs. (10) and (11)

$$\text{rate} = -\frac{d[\text{olefin}]}{dt} = -k[\text{FAC}]_0^n[\text{olefin}] = -k_{\text{obs}}[\text{olefin}] \quad (10)$$

$$k_{\text{obs}} = k[\text{FAC}]_0^n \quad (11)$$

where k represents the second-order rate constant for the reaction of FAC with an olefin; k_{obs} is the observed pseudo-first-order rate constant for reaction of FAC with an olefin; $[\text{FAC}]_0$ represents the initial FAC concentration; and n represents the reaction order in FAC. A log transformation of Eq. (11) yields Eq. (12)

$$\log_{\text{obs}} = n(\log[\text{FAC}]_0) + \log k \quad (12)$$

The reaction order in FAC (i.e., values of n) can be determined via linear regressions of $\log k_{\text{obs}}$ vs $\log [\text{FAC}]_0$.

k_{obs} for selected olefins (5.0 μM) in the presence of different $[\text{FAC}]_0$ (0.1–6.0 mM) under pseudo first-order conditions at pH 7.5 were measured and are shown in Fig. 2. k_{obs} increases with increasing $[\text{FAC}]_0$, and the resulting n values range from 1.0 ± 0.2 (for MCA and 4-Cl-α-CNCA) to 2.1 ± 0.07 (for 4-Cl CA) (Figure S5, SI). For most of the olefins, n values are ≥ 1.4 . Similar trends were also observed for reactions of aromatic ethers (Sivey et al., 2012) and dimethenamid (Sivey et al., 2010) with FAC, which can be explained by the combined contributions of different chlorine species to the overall chlorine reactivity.

The reaction is second-order in [HOCl] (i.e., $n=2$) if Cl₂O is the predominant reactive chlorine species, as $[\text{Cl}_2\text{O}]$ is proportional to $[\text{HOCl}]^2$ (i.e., $[\text{Cl}_2\text{O}] = K_2[\text{HOCl}]^2$, Eq. (2)). Furthermore, a disguised second-order dependence on [HOCl] can be observed if FAC solutions contain approximately equimolar concentrations of HOCl and Cl[−] (i.e., $[\text{Cl}_2] = K_3[\text{HOCl}][\text{Cl}^-][\text{H}^+] \approx K_3[\text{HOCl}]^2[\text{H}^+]$ when $[\text{HOCl}] \approx [\text{Cl}^-]$, Eq. (3)) (Lau et al., 2016). Indeed, ion chromatography analyses showed that $[\text{Cl}^-]$ in the FAC solution were about 1.7 times the [HOCl], and this level of $[\text{Cl}^-]$ ($[\text{Cl}^-]_{\text{baseline}}$) was considered for reaction solutions without extra addition of Cl[−]. Hence, the obtained n values (ranging from ~1 to ~2) likely resulted from the combined contribution of HOCl, Cl₂O, and Cl₂. Therefore, k_{obs} for the chlorination of olefins can be expressed as Eq. (13)

$$k_{\text{obs}} = k_{\text{HOCl}}[\text{HOCl}] + k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] + k_{\text{Cl}_2}[\text{Cl}_2] \quad (13)$$

where k_{HOCl} , $k_{\text{Cl}_2\text{O}}$, and k_{Cl_2} represent the species-specific second-order rate constants (M^{−1}s^{−1}) for the reactions of HOCl, Cl₂O, and Cl₂ with olefins, respectively.

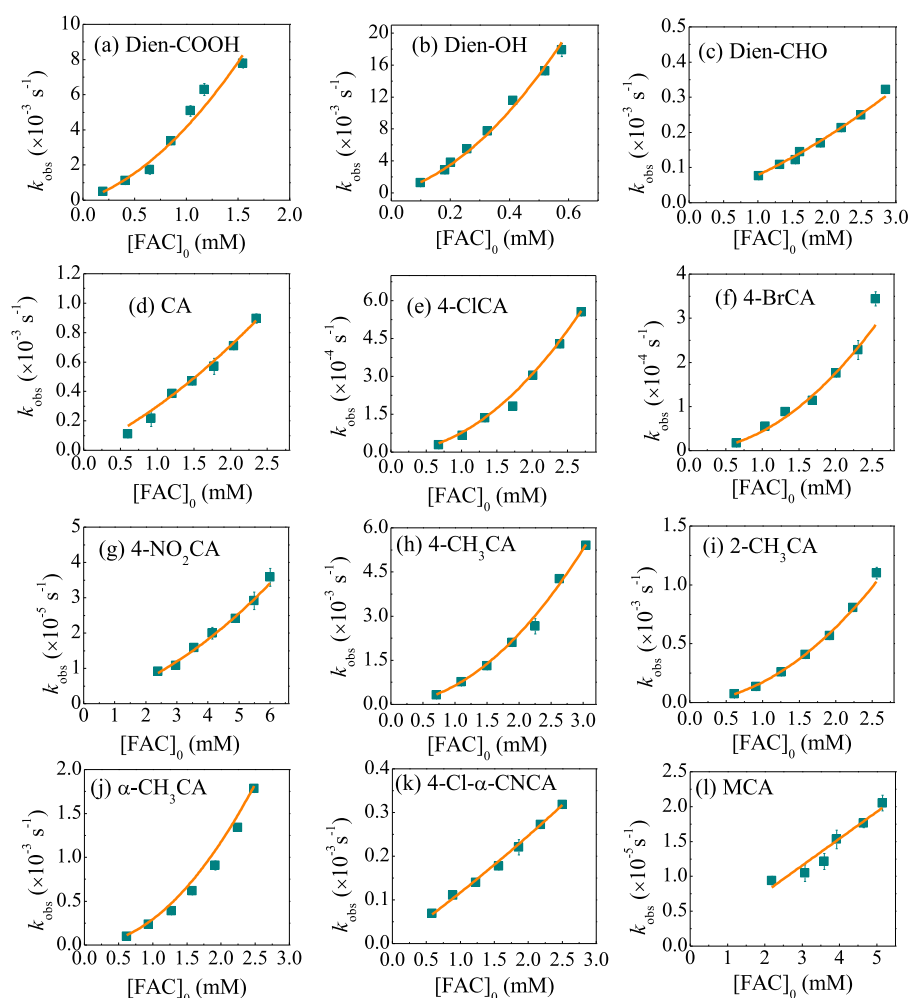


Fig. 2. Observed pseudo first-order rate constants (k_{obs}) for the reactions of selected olefins (see Fig. 1 for abbreviations) with FAC as a function of the initial FAC concentration at pH 7.5. The symbols represent the experimental data and the lines represent model predictions by fitting data of k_{obs} with nonlinear least-squares regressions based on Eq. (15). Experimental conditions: [olefins] = 5 μM , $[\text{FAC}]_0 = 0.1\text{--}6.0$ mM, pH = 7.5.

3.1.2. Chlorination kinetics of Dien-COOH and CA

Role of Cl_2 for the oxidation of organic compounds. Previous studies show that Cl_2 usually plays an important role at pH < 7.5 in the presence of high Cl^- concentrations, while Cl_2O is non-negligible at neutral pH (Sivey et al., 2010, 2012; Lau et al., 2016). Based on literature data, the fractions of HOCl ($f(\text{HOCl})$, Eq. (14a)), Cl_2O ($f(\text{Cl}_2\text{O})$, Eq. (14b)), and Cl_2 ($f(\text{Cl}_2)$, Eq. (14c)) to the transformation of selected target compounds by FAC under our experimental conditions (i.e., $[\text{FAC}] = 0.1\text{--}6.0$ mM, $[\text{Cl}^-]_{\text{baseline}} = 1.7$ [HOCl] $_0$, pH = 7.5) were calculated with the reported species-specific second-order rate constants and are provided in Figure S6 (SI).

$$f(\text{HOCl}) = \frac{k_{\text{HOCl}}[\text{HOCl}]}{k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] + k_{\text{HOCl}}[\text{HOCl}] + k_{\text{Cl}_2}[\text{Cl}_2]} \quad (14a)$$

$$f(\text{Cl}_2\text{O}) = \frac{k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}]}{k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] + k_{\text{HOCl}}[\text{HOCl}] + k_{\text{Cl}_2}[\text{Cl}_2]} \quad (14b)$$

$$f(\text{Cl}_2) = \frac{k_{\text{Cl}_2}[\text{Cl}_2]}{k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] + k_{\text{HOCl}}[\text{HOCl}] + k_{\text{Cl}_2}[\text{Cl}_2]} \quad (14c)$$

Cl_2 contributes <5% at $[\text{FAC}]_0$ of 0.1 mM, while it becomes increasingly important with increasing $[\text{FAC}]_0$ for each compound. $f(\text{Cl}_2)$ remains <20% for the majority of the compounds (except for two chlorophenols and one cyclic olefin) at pH 7.5 even at $[\text{FAC}]_0$ of 6.0 mM (the maximum $[\text{FAC}]_0$ used in this study). Even though

the contribution of Cl_2 seems to be generally low, its relevance for chlorination of olefins at pH 7.5 was investigated for Dien-COOH and CA as representative aliphatic and aromatic olefins, respectively.

Determination of kinetic parameters for chlorination of Dien-COOH and CA. The impact of the Cl^- concentration (0–20 mM) on the chlorination kinetics of Dien-COOH and CA at pH 5 were investigated. As shown in Fig. 3, k_{obs} for both Dien-COOH and CA increase linearly with increasing Cl^- concentrations. k_{obs} for Dien-COOH in the presence of 10 mM Cl^- is almost 40 times higher than the value without addition of Cl^- ($[\text{Cl}^-]_{\text{baseline}} = 1.7$ [FAC] $_0$, i.e., 0.31 and 1.02 mM for Dien-COOH and CA, respectively). Similar observations were also reported during chlorination of phenols (Lau et al., 2016), alkenes (Lau et al., 2019), and *p*-xylene (Voudrias et al., 1988a, b), which was attributed to the reaction of Cl_2 . Based on Eq. (3), the formation of Cl_2 is favored in the presence of Cl^- at lower pH. k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$ for Dien-COOH and CA could be obtained by fitting the experimental data in Fig. 2 (2(a) for Dien-COOH and 2(d) for CA) and Fig. 3 with Eq. (13) following a similar protocol as reported in the literature (Lau et al., 2019) (SI, Text S3 and Figure S7 for more information). The experimental data could be well fitted (lines in Fig. 2(a), 2(d), and Fig. 3) and the obtained $k_{\text{Cl}_2\text{O}}$ and k_{Cl_2} were $(9.9 \pm 1.5) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and $(1.1 \pm 0.2) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for Dien-COOH; and $(2.6 \pm 0.8) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and $(4.2 \pm 0.1) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ for CA, respectively (Table 1).

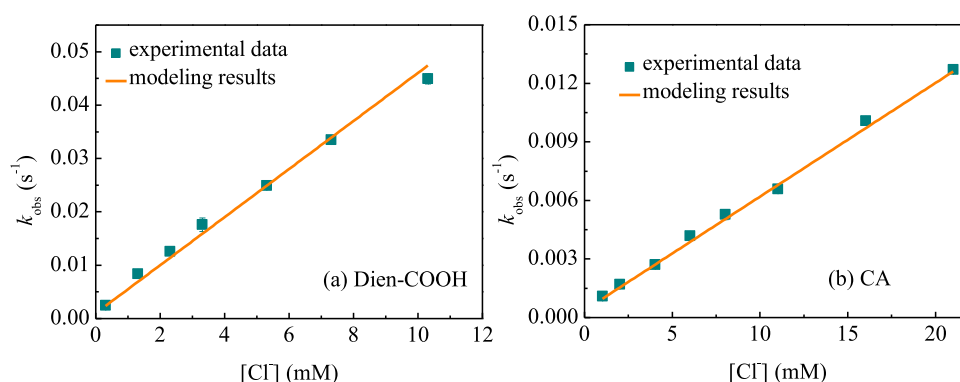


Fig. 3. Impacts of the Cl^- concentration on the observed pseudo first-order rate constants (k_{obs}) for the chlorination of (a) Dien-COOH and (b) CA at pH 5.0. Experimental conditions: (a) $[\text{Dien-COOH}] = 5 \mu\text{M}$, $[\text{FAC}]_0 = 180 \mu\text{M}$, $[\text{Cl}^-]_{\text{dosed}} = 0\text{--}10 \text{ mM}$; (b) $[\text{CA}] = 5 \mu\text{M}$, $[\text{FAC}]_0 = 600 \mu\text{M}$, $[\text{Cl}^-]_{\text{dosed}} = 0\text{--}20 \text{ mM}$. Inherent Cl^- concentration (i.e., $[\text{Cl}^-]_{\text{dosed}} = 0 \mu\text{M}$) equals to 1.7 times of $[\text{FAC}]_0$. The symbols represent the experimental results and the lines represent the modeled predictions based on Eq. (13) by including k_{HOCl} , $k_{\text{Cl}_2\text{O}}$, and k_{Cl_2} from Table 1.

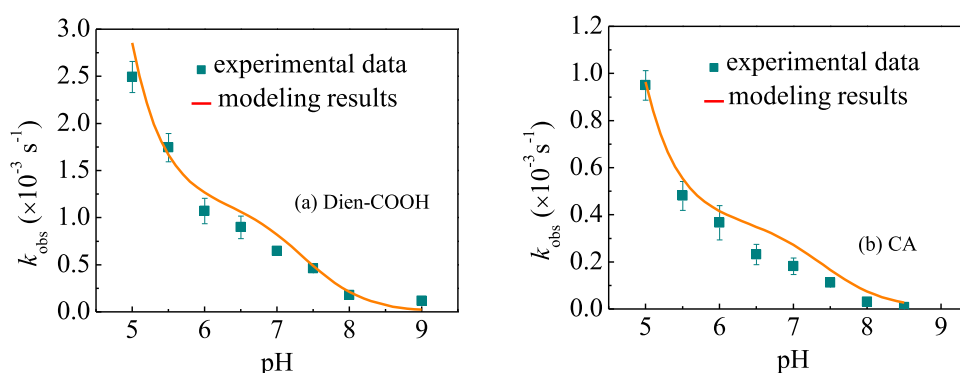


Fig. 4. pH-dependence of the observed pseudo first-order rate constants (k_{obs}) for the reactions of selected olefins with FAC as a function of pH for (a) Dien-COOH and (b) CA. Experimental conditions: (a) $[\text{Dien-COOH}] = 5 \mu\text{M}$, $[\text{FAC}]_0 = 180 \mu\text{M}$; (b) $[\text{CA}] = 5 \mu\text{M}$, $[\text{FAC}]_0 = 600 \mu\text{M}$. The symbols represent the experimental results and the lines represent the modeled predictions based on Eq. (13) by including k_{HOCl} , $k_{\text{Cl}_2\text{O}}$, and k_{Cl_2} from Table 1.

Overall, Cl_2O and Cl_2 have comparable reactivities towards Dien-COOH and CA (within a factor of 2). The concentrations of HOCl , Cl_2O , and Cl_2 at pH 7.5 were calculated as a function of the initial FAC concentrations (Text S1, SI) and are shown in Figure S1b (SI). Within the investigated FAC concentration ranges (0.1–6.0 mM), HOCl is by far the dominant chlorine species, followed by Cl_2O with a concentration nearly 35 times higher than that of Cl_2 . Therefore, the low calculated concentration of Cl_2 leads to only a small contribution ($f(\text{Cl}_2) < 5\%$) to the chlorination of Dien-COOH and CA at pH 7.5 in Fig. 2 (Figures S8a–S8b, SI).

pH-dependence of chlorination of Dien-COOH and CA. The kinetics of the chlorination of Dien-COOH and CA were investigated in the pH range of 5.0–8.5. k_{obs} for Dien-COOH and CA showed a strong pH-dependence, with a decreasing trend as the pH increased (Fig. 4). The pH dependence of k_{obs} for Dien-COOH and CA was fitted by Eq. (13) with the obtained values for k_{HOCl} , $k_{\text{Cl}_2\text{O}}$, and k_{Cl_2} (Table 1). A fairly good agreement between the experimental (squares in Fig. 4) and calculated results (lines in Fig. 4) was obtained for both Dien-COOH and CA. $f(\text{HOCl})$, $f(\text{Cl}_2\text{O})$, and $f(\text{Cl}_2)$ for the chlorination of Dien-COOH and CA in the investigated pH range are shown in Figures S8c–S8d (SI). $f(\text{Cl}_2)$ was ~60% at pH 5 for both Dien-COOH and CA, and decreased to <5% at pH 7. Cl_2O played an important role at circum-neutral pH with $f(\text{Cl}_2\text{O}) \leq 20\%$ for both Dien-COOH and CA, while $f(\text{Cl}_2\text{O})$ decreased significantly at lower and higher pH. $f(\text{HOCl})$, $f(\text{Cl}_2\text{O})$, and $f(\text{Cl}_2)$ for Dien-COOH and CA as a function of pH under typical drinking water chlorination conditions were also calculated and are shown in Figures S8e–S8f (SI). The importance of Cl_2 decreased as the pH increased with $f(\text{Cl}_2)$ decreasing from >30% at pH 5 to <2% at pH 7.5 for both olefins.

Though $f(\text{Cl}_2\text{O})$ reached the maximum at neutral pH, it was <5% in the pH range investigated. These results suggest that Cl_2 tends to contribute to the chlorination kinetics of olefins in the presence of Cl^- at lower pH ($\text{pH} \leq 6.0$), while Cl_2O plays a more significant role in the pH range of $6.0 < \text{pH} \leq 7.5$ at high FAC concentrations. However, for conditions relevant for drinking water, the contributions of Cl_2 and Cl_2O for the reactions with Dien-COOH and CA are typically low (Figures S8e–S8f, SI).

3.1.3. Contributions of HOCl and Cl_2O to the oxidation of selected olefins by FAC

Determination of kinetic parameters. The above results suggest that Cl_2 contributes only slightly to the chlorination kinetics of olefins at $\text{pH} > 6.0$. Therefore, to simplify the modeling process, Eq. (13) was adapted to Eq. (15) by excluding the Cl_2 reactions for $\text{pH} > 6.0$.

$$k_{\text{obs}} = k_{\text{HOCl}}[\text{HOCl}] + k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] \quad (15)$$

Second-order rate constants for the reactions of HOCl (k_{HOCl}) and Cl_2O ($k_{\text{Cl}_2\text{O}}$) with olefins were computed by fitting data of k_{obs} (Fig. 2) with nonlinear least-squares regressions based on Eq. (15). The k_{obs} data for each olefin at pH 7.5 is well predicted (lines in Fig. 2) and the corresponding values for k_{HOCl} and $k_{\text{Cl}_2\text{O}}$ are compiled in Table 1. For each of the selected olefins (except for MCA), $k_{\text{Cl}_2\text{O}}$ was 4–6 orders of magnitude higher than k_{HOCl} . $f(\text{Cl}_2\text{O})$ and $f(\text{HOCl})$ to the overall transformation of olefins by FAC under our experimental conditions were calculated by the second-order rate constants in Table 1 and are presented in Figure S9 (SI). Overall, $f(\text{Cl}_2\text{O})$ increases gradually with increasing $[\text{FAC}]_0$. At pH 7.5,

Table 1

Species-specific second-order rate constants ($M^{-1}s^{-1}$) for the reactions of chlorine ($HOCl$ and Cl_2O) (based on Eq. (15) with data from Fig. 2) and bromine ($HOBr$ and Br_2O) (based on Eq. (17) with data from Fig. 6) with olefins as well as the half-lives ($t_{1/2}$) of olefins for typical drinking water chlorination conditions. The values for k_{Cl_2} of Dien-COOH and CA were calculated with Eq. (13) from the data in Figs 2 and 3.

olefins	k_{Cl_2O}	k_{HOCl}	k_{Cl_2}	k_{Br_2O}	k_{HOBr}	Typical drinking water chlorination conditions ^b				
						$t_{1/2}$		contribution of chlorine species (%)		
						(h)	(day)	f($HOCl$)	f(Cl_2O)	f(Cl_2)
Dien-COOH	$(9.9 \pm 1.5) \times 10^5$	4.0 ± 0.6	$(1.1 \pm 0.2) \times 10^6$	$(2.5 \pm 0.08) \times 10^5$	$(1.1 \pm 0.3) \times 10^2$	3.3	0.1	96.6	2.9	0.5
Dien-OH	$(1.8 \pm 0.1) \times 10^7$	19.0 ± 1.5	N.D.	$(1.8 \pm 0.04) \times 10^7$	$(1.1 \pm 0.6) \times 10^3$	0.6	0.03	89.6	10.4	
Dien-CHO	$(6.8 \pm 0.9) \times 10^3$	0.1 ± 0.01	N.D.	$(1.7 \pm 0.06) \times 10^2$	0.7 ± 0.02	136.4	5.7	99.2	0.8	
CA	$(2.6 \pm 0.8) \times 10^4$	0.5 ± 0.1	$(4.2 \pm 0.1) \times 10^4$	$(2.2 \pm 0.04) \times 10^4$	$< 5.0^a$	27.3	1.1	99.2	0.6	0.2
4-ClCA	$(3.6 \pm 0.2) \times 10^4$	$< 0.08^a$	N.D.	$(3.1 \pm 0.3) \times 10^3$	0.3 ± 0.3	163.1	6.8	94.9	5.1	
4-BrCA	$(2.0 \pm 0.3) \times 10^4$	$< 0.04^a$	N.D.	$(4.0 \pm 0.2) \times 10^3$	0.5 ± 0.3	323.9	13.5	94.2	5.8	
4-CH ₃ CA	$(2.6 \pm 0.04) \times 10^5$	0.2 ± 0.04	N.D.	$(9.7 \pm 0.4) \times 10^4$	$< 25.0^a$	59.4	2.5	86.3	13.7	
2-CH ₃ CA	$(6.7 \pm 0.2) \times 10^4$	0.1 ± 0.01	N.D.	$(2.7 \pm 0.09) \times 10^4$	$< 6.0^a$	127.1	5.3	92.4	7.6	
4-NO ₂ CA	$(2.6 \pm 0.4) \times 10^2$	$(4.5 \pm 0.7) \times 10^{-3}$	N.D.	6.9 ± 0.8	$(7.9 \pm 2.8) \times 10^{-3}$	3034.8	126.4	99.3	0.7	
α -CH ₃ CA	$(1.4 \pm 0.8) \times 10^5$	$< 0.5^a$	N.D.	$(9.4 \pm 0.8) \times 10^3$	1.4 ± 0.5	26.6	1.1	97.7	3.3	
4-Cl- α -CNCA	$(3.1 \pm 1.1) \times 10^3$	0.2 ± 0.01	N.D.	$< 1.5^a$	$(2.6 \pm 0.1) \times 10^{-2}$	68.6	2.8	99.8	0.2	
MCA	$< 95^a$	$(7.7 \pm 0.2) \times 10^{-3}$	N.D.	10.0 ± 0.6	$(4.9 \pm 2.0) \times 10^{-3}$	1783.4	74.3	99.8	0.2	

(a): the modeled results for these values based on Eq. (15) and Eq. (17) were 0. These maximum values were obtained by manual fitting (Text S4 and Figure S10, SI); (b): pH=7.5, [FAC] = 2.0 mg/L \approx 28 μ M, [Cl⁻] = 8 mg/L \approx 0.23 mM; N.D.: not determined in this study.

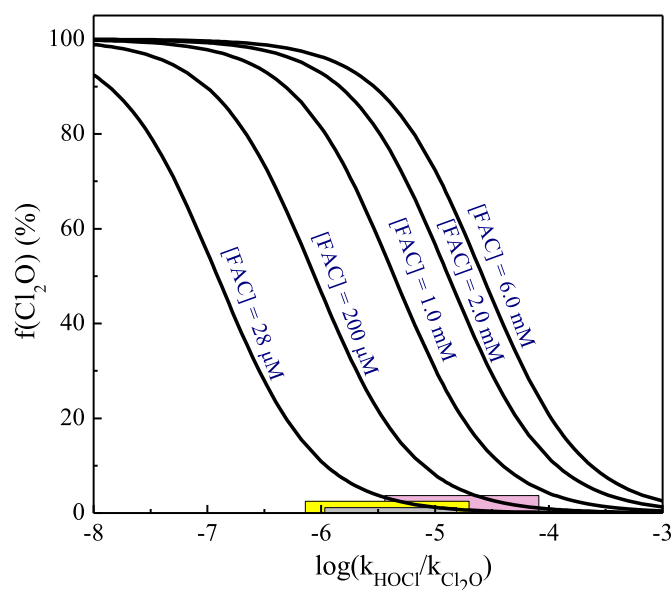


Fig. 5. Calculated fractions of Cl_2O ($f(Cl_2O)$) to the total extent of chlorination of target compounds as a function of the k_{HOCl}/k_{Cl_2O} for different FAC concentrations at pH 7.5 based on Eq. (16), where $[HOCl]$ approximately equals to 0.5 [FAC]. The gray, yellow, and pink squares represent the k_{HOCl}/k_{Cl_2O} ranges for the selected aliphatic olefins, CA and its derivatives with substituents at the benzene ring, and CA derivatives with substituents at the double bond and cinnamic ester, respectively.

$f(Cl_2O)$ was $>50\%$ for olefins such as 4-ClCA, 4-BrCA, and α -CH₃CA. In contrast, for olefins such as Dien-CHO, 4-Cl- α -CNCA, and MCA, $f(HOCl)$ dominated at pH 7.5.

Chlorination under realistic conditions. $f(Cl_2O)$ and $f(HOCl)$ for the transformation of selected olefins by FAC as well as the half-lives ($t_{1/2}$) of olefins at pH 7.5 for typical drinking water chlorination conditions were calculated and are presented in Table 1. $HOCl$ contributes the most to the transformation of all the selected olefins with $f(HOCl)$ generally $>85\%$, while Cl_2O contributes $<10\%$ (except for Dien-OH (10.4%) and 4-CH₃CA (13.7%)). These observations are different from the results obtained under the laboratory conditions above, for which Cl_2O plays an equal or more significant role compared to $HOCl$ (Figure S9, SI). This discrepancy is due to the lower concentration of FAC applied for typical drinking water chlorination conditions (i.e., [FAC] = 2.0 mg/L as $Cl_2 \approx 28 \mu$ M), leading to much lower Cl_2O concentrations (Figure S1, SI). Overall, $f(Cl_2O)$ to the transformation of olefins by chlorine is mainly determined by two factors, (i) the relative reactivities of $HOCl$ and Cl_2O towards olefins ($\frac{k_{HOCl}}{k_{Cl_2O}}$); and (ii) the $HOCl$ concentration (Eq. (16), originating from Eq. (14b) by excluding the negligible contribution of Cl_2).

$$f(Cl_2O) = \frac{k_{Cl_2O}[Cl_2O]}{k_{Cl_2O}[Cl_2O] + k_{HOCl}[HOCl]} = \frac{k_{Cl_2O}K_2[HOCl]^2}{k_{Cl_2O}K_2[HOCl]^2 + k_{HOCl}[HOCl]} = \frac{1}{1 + \frac{k_{HOCl}}{k_{Cl_2O}K_2[HOCl]}} \quad (16)$$

$f(Cl_2O)$ were calculated as a function of k_{HOCl}/k_{Cl_2O} (10^{-8} – 10^{-3}) for various FAC concentrations ([FAC] = 0.028–6.0 mM) (Fig. 5). $f(Cl_2O)$ increases with increasing reactivity of Cl_2O (i.e., decreasing k_{HOCl}/k_{Cl_2O}) for each $HOCl$ concentration. A higher $f(Cl_2O)$ can be calculated at higher $HOCl$ concentrations for a fixed k_{HOCl}/k_{Cl_2O} .

The $t_{1/2}$ during chlorination ([FAC] = 2.0 mg/L as $Cl_2 \approx 28 \mu$ M) of the selected olefins varies from <40 min (for Dien-OH) to >126 days (for 4-NO₂CA) with values ≥ 1.1 days for most of the olefins. This result indicates that chlorination will only lead to a partial

abatement of the selected olefins in drinking water treatment and distribution systems.

3.2. Bromination of olefins

3.2.1. Kinetics of bromine reactions with olefins

Plots of $\ln([\text{olefins}]_t/[\text{olefins}]_0)$ obtained under pseudo-first-order conditions (i.e., $[\text{bromine}]_0/[\text{olefin}]_0 > 10$) displayed linear relationships as a function of the reaction time (Figure S11, SI), suggesting that the reactions of bromine with olefins are first-order in olefins. k_{obs} for bromine reactions with olefins (3 μM) increases with increasing initial bromine concentrations ($[\text{HOBr}]_0$, 0.03–0.85 mM) at pH 7.5 (Fig. 6). The corresponding reaction order in bromine was obtained by plotting $\log(k_{\text{obs}})$ vs $\log([\text{bromine}]_0)$ as outlined above. The slope n was in the range of 1.0 ± 0.06 (for 4-Cl- α -CNCA) to 1.9 ± 0.04 (for Dien-OH) for the investigated conditions (Figure S12, SI) with $n > 1.4$ for most of the selected olefins. These results indicate that bromine species other than HOBr contribute to the transformation of olefins.

3.2.2. Contributions of HOBr and Br₂O

Based on the assessment above and the production of HOBr solutions by reaction of Br[−] with excess ozone, the presence of Br₂ can be excluded for our experimental systems. Therefore, only HOBr and Br₂O will be considered in this manuscript. Br₂O which is in equilibrium with HOBr (Eq. (6)) generally exhibits higher reactivities towards organic compounds than HOBr, and it can play important roles in the transformation of organic compounds (Sivey et al., 2013, 2015). The high reaction order ($n \geq 1.4$ except for 4-Cl- α -CNCA) in bromine under our experimental conditions is likely due to the contributions of Br₂O because this species is proportional to $[\text{HOBr}]^2$ (Eq. (6)). Accordingly, the observed first-order rate constants for the reactions of bromine with olefins can be interpreted by Eq. (17):

$$k_{\text{obs}} = k_{\text{HOBr}}[\text{HOBr}] + k_{\text{Br}_2\text{O}}[\text{Br}_2\text{O}] \quad (17)$$

k_{HOBr} and $k_{\text{Br}_2\text{O}}$ represent the species-specific second-order rate constants for reactions of HOBr and Br₂O with an olefin, respectively.

k_{HOBr} and $k_{\text{Br}_2\text{O}}$ values were obtained by fitting k_{obs} in Fig. 6 with Eq. (17) via non-linear least-squares regressions. The experimental data were well fitted (lines in Fig. 6) and the obtained values for k_{HOBr} and $k_{\text{Br}_2\text{O}}$ are compiled in Table 1. For most of the selected olefins (except for 4-Cl- α -CNCA), $k_{\text{Br}_2\text{O}}$ is 3–4 orders of magnitude higher than k_{HOBr} (< 0.01 – $> 10^3 \text{ M}^{-1}\text{s}^{-1}$). The fractions of HOBr ($f(\text{HOBr})$) and Br₂O ($f(\text{Br}_2\text{O})$) to the overall transformation of olefins under the investigated conditions are shown in Figure S13 (SI). The relative importance of Br₂O to the overall reactivity increased with increasing $[\text{HOBr}]_0$. Br₂O was the dominant reactive species for the bromination of Dien-OH, CA, 4-CICA, 4-BrCA, 4-CH₃CA, 2-CH₃CA, and α -CH₃CA with $f(\text{Br}_2\text{O}) > 50\%$, in accordance with the higher reaction order in bromine ($n > 1.5$) therein. For Dien-CHO and 4-NO₂CA, HOBr also played a non-negligible role in their transformation, while for 4-Cl- α -CNCA, HOBr was the primary bromine species.

Moreover, it seems that Cl₂O is generally more reactive towards olefins than Br₂O (Table 1). For instance, $k_{\text{Cl}_2\text{O}}$ for Dien-COOH ($9.9 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$), 4-BrCA ($2.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$), and α -CH₃CA ($1.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) are much higher than $k_{\text{Br}_2\text{O}}$, i.e., $2.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for Dien-COOH, $4.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ for 4-BrCA, and $9.4 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ for α -CH₃CA, respectively. In comparison, HOBr is more reactive towards selected olefins than HOCl (Table 1), as has been widely documented in the literature (Heeb et al., 2014). A similar trend was also reported for the reactions of different chlorine and bromine species with dimethenamid following the order of HOCl < HOBr < Br₂O < Cl₂O \approx Cl₂ < BrOCl \approx Br₂ <

BrCl, which was explained by the differences in nucleofugality and polarizability of these halogen species (Sivey et al., 2013). Though BrOCl, Br₂, and BrCl are not present in our bromine solution, they are also likely to contribute to the transformation of olefins during chlorination of Br[−]-containing waters under certain conditions.

3.3. Effects of substituents on the kinetics of the reactions of FAC and bromine with olefins and linear free energy relationship (LFER)

3.3.1. Effects of substituents on the kinetics of FAC reactions with olefins

Aliphatic olefins. The species-specific second-order rate constants in Table 1 demonstrate that substituents play a significant role in the chlorination of olefins. For aliphatic olefins, the second-order rate constants for the reactions with Cl₂O decreased in the order of Dien-OH ($(1.8 \pm 0.1) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) > Dien-COOH ($(9.9 \pm 1.5) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) > Dien-CHO ($(6.8 \pm 0.9) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$). A similar trend was observed for k_{HOCl} with Dien-OH ($19.0 \pm 1.5 \text{ M}^{-1}\text{s}^{-1}$) > Dien-COOH ($4.0 \pm 0.6 \text{ M}^{-1}\text{s}^{-1}$) > Dien-CHO ($0.1 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$). The smaller electron-withdrawing effect of the OH- than the COOH- group leads to a higher electron density in the conjugated double bonds of Dien-OH compared to Dien-COOH (Lee and von Gunten, 2012), which enhances its reactivity with electrophiles such as Cl₂O (a factor of 10) and HOCl (a factor of 5). A substitution by an aldehyde as in Dien-CHO leads to an electron deficiency and results in a lower chlorine reactivity than Dien-COOH (a factor of 10^2), because -CHO is a stronger electron-withdrawing group than -COO[−] (deprotonated form of Dien-COOH is the major species (pKa = 4.75 (Arya, 1980)) at pH 7.5) as suggested by their Taft constants ($\sigma^* = 2.15$ and -1.06 for -CHO and -COO[−], respectively (Lee and von Gunten, 2012)).

Aromatic olefins. For aromatic olefins including CA and its derivatives, substituents at both the benzene ring and at the olefin bond were investigated (Fig. 1 and Table 1). Furthermore, a cinnamic acid methyl ester was investigated. HOCl shows very low reactivities towards CA and its derivatives with $k_{\text{HOCl}} < 1.0 \text{ M}^{-1}\text{s}^{-1}$, wherefore, the substituent effects are mainly discussed based on olefin reactions with Cl₂O. $k_{\text{Cl}_2\text{O}}$ for CA derivatives (with substituents at the benzene ring) decrease in the order of 4-CH₃CA \approx 2-CH₃CA > CA \approx 4-CICA \approx 4-BrCA \gg 4-NO₂CA. The methyl group as an electron-donor (i.e., Hammett constants σ^+ for 4-CH₃- and 2-CH₃- groups are -0.306 and -0.210 , respectively) (Lee and von Gunten, 2012) increases the electron density on the benzene ring, which may activate the double bond via an inductive effect. Therefore, a higher k_{app} for the reactions of Cl₂O with 4-CH₃CA and 2-CH₃CA compared to the unsubstituted CA (a factor of 3–10) were obtained. The substitution of electron-withdrawing halogen substituents (Cl- and Br-) at the para position of the benzene ring of CA displays slight effects on its reactivity towards Cl₂O. Comparatively, substitution by a NO₂-group remarkably decreased the second-order rate constant for the reaction of 4-NO₂CA with Cl₂O by a factor of 100 compared to CA. These results are likely due to the stronger electron-withdrawing properties of the NO₂-group as indicated by its larger Hammett constant (i.e., σ^+ for NO₂-, Cl-, and Br- groups are 0.777, 0.112, and 0.148, respectively) (Lee and von Gunten, 2012), which leads to a significantly greater impact on the olefin bond than the Cl- and Br-groups (Fang et al., 1958; Butt and Topsom, 1980; Wang and Chen, 2020). Similar results were also reported by Aruna and Manikyamba (1995), where 4-CICA and CA showed comparable reactivities towards quinolinium dichromate with both of them reacting much more readily than 4-NO₂CA.

Moreover, substituents on the CA double bond also showed significant impact on the reactivity of aromatic olefins towards Cl₂O. $k_{\text{Cl}_2\text{O}}$ for the reaction of α -CH₃CA with Cl₂O was 10 times higher compared to CA, while $k_{\text{Cl}_2\text{O}}$ for the reaction of 4-Cl- α -CNCA with Cl₂O was nearly 10 times lower compared to 4-CICA (Table 1).

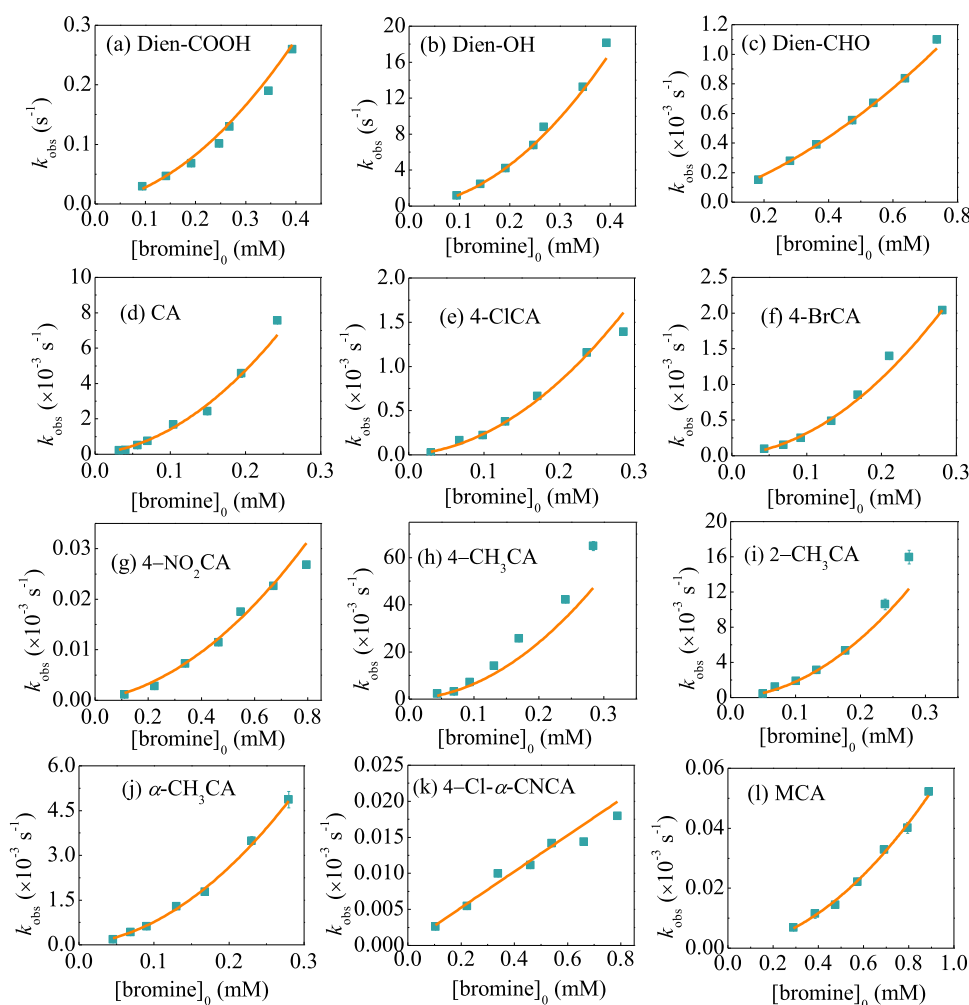


Fig. 6. Observed pseudo first-order rate constants (k_{obs}) for the reactions of selected olefins (see Fig. 1 for abbreviations) with bromine as a function of the initial bromine concentration at pH 7.5. The symbols represent the experimental results and the lines represent the modeled predictions by fitting data of k_{obs} with nonlinear least-squares regressions based on Eq. (17). Experimental conditions: [olefins] = 3 μM , [bromine]₀ = 0.03–0.85 mM, pH = 7.5.

These observations can be explained by the electron-donating effect of the methyl group in $\alpha\text{-CH}_3\text{CA}$, which increases the electron density of the double bond. In contrast, the cyano group in 4-Cl- $\alpha\text{-CNCA}$ reduced the electron density of the double bond due to its electron-withdrawing character (Lee and von Gunten, 2012). For MCA, Cl_2O displayed a much lower reactivity compared to CA due to the ester group in MCA, which is expected to decrease the electron density via its electron-withdrawing effect (Lee and von Gunten, 2012).

3.3.2. Effects of substituents on the kinetics of bromine reactions with olefins

Similar substitution effects for the kinetics of the reactions of bromine and chlorine with olefins were obtained, i.e., electron-donating groups (i.e., OH- and CH_3 -) generally enhance the reactivities (a factor of 3–100), while electron-withdrawing groups (i.e., COOH-, CHO-, Cl-, Br-, NO_2 -, CN-, and -COOR) lead to lower second-order rate constants (a factor of 10–10000) (Table 1).

3.3.3. LFER

A LFER for the reactions of CA and its derivatives with $\text{Cl}_2\text{O}/\text{Br}_2\text{O}$ was developed. A previous study showed that Taft constants σ^* were the most suitable descriptors for establishing LFER relationships for olefin reactions with ozone (Lee and von Gun-

ten, 2012). An attempt was made to establish a relationship between $k_{\text{Cl}_2\text{O}}$ or $k_{\text{Br}_2\text{O}}$ for selected olefins vs Taft σ^* but it was impossible due to the lack of Taft σ^* for most of the substituents on the olefins. In contrast, a reasonable correlation between $\log(k_{\text{Cl}_2\text{O}})$ or $\log(k_{\text{Br}_2\text{O}})$ and Hammett σ^+ for the reaction of Cl_2O or Br_2O with CA derivatives (with substituents at the benzene ring) could be established (Figures S14a–S14b, SI). Negative slopes (ρ) were obtained for both cases with -2.6 ± 0.3 ($R^2 = 0.95$) for Cl_2O and -3.8 ± 0.3 ($R^2 = 0.96$) for Br_2O . The more negative ρ value for Br_2O than for Cl_2O indicates that Br_2O is more sensitive to substituent effects. Moreover, the LFER between $\log(k_{\text{Cl}_2\text{O}})$ or $\log(k_{\text{Br}_2\text{O}})$ vs Hammett σ^+ by excluding 4- NO_2CA was also assessed. Acceptable correlations ($R^2 = 0.76$ and 0.84 for Cl_2O and Br_2O , respectively, Figures S14c–S14d, SI) were obtained with a similar trend as observed by including 4- NO_2CA (Figure S14a–S14b, SI). These results confirm that though 4- NO_2CA as an end member tends to dominate the correlation (Figures S14a–S14b, SI), it does not affect the final conclusion.

3.4. Transformation products

The transformation products from the reaction of FAC (600 μM) with CA (5 μM) at pH 5.0 were analyzed by HPLC/HRMS in both (ESI (+)) and (ESI (-)) mode. Three transformation products (TPs

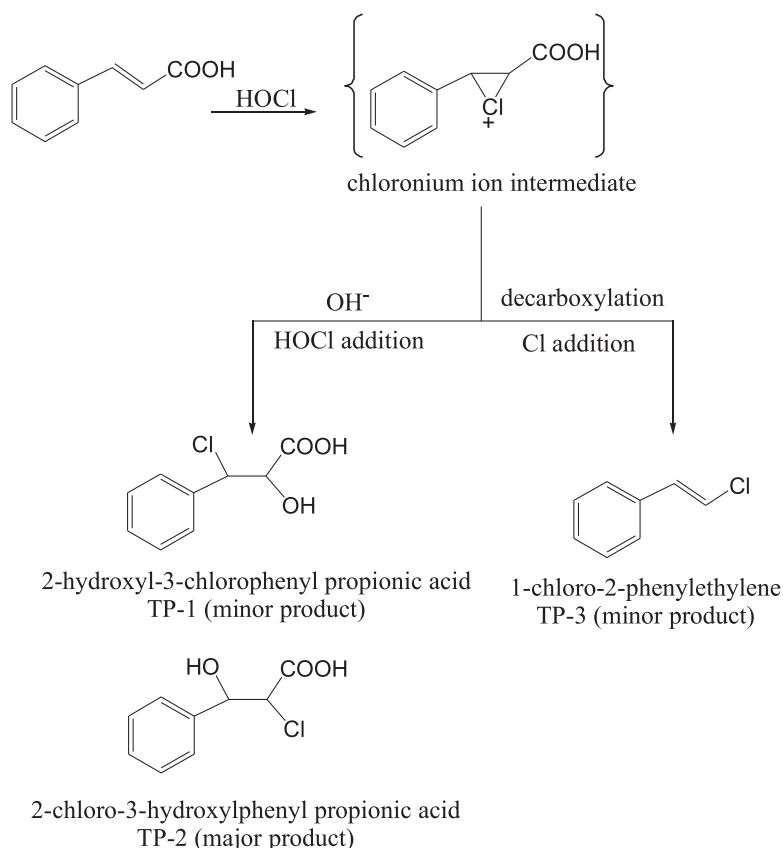


Fig. 7. Proposed mechanism for the reaction of HOCl with CA at pH 5.0. For a discussion of the transformation products see text and Figures S15-S17 in SI.

1-3) were detected with elution times of 12.92, 14.38, and 19.10 min for TP-1, TP-2, and TP-3, respectively (Figures S15a-S15b, SI). TP-1 and TP-2 identified at ESI(-) mode have the same molecular ion of m/z 199.0168, suggesting that they are structural isomers. They are assigned to $C_9H_8O_3Cl$ ($[M-H]^-$) based on their fragment ions of 163.0401($C_9H_7O_3$, $[M-HCl]^-$) and 119.0503(C_8H_7O , $[M-HCl-COO]^-$) (Figure S16, SI) and their chlorine isotopic patterns (i.e., $^{35}Cl/^{37}Cl = 3/1$, Figure S17, SI), corresponding to HOCl-adduct products of CA ($C_9H_8O_2$). The higher response of peak TP-2 compared to TP-1 (Figure S15a, SI) indicated that TP-2 might be the major product. TP-3 with a molecular ion of m/z 139.0314 ($[M+H]^+$) was identified at ESI (+) with a minor peak (Figure S15b, SI) and was assigned to C_8H_7Cl , corresponding to a Cl-adduct product of the decarboxylated CA. It has been reported that addition of HOCl or HOBr at the olefin β -carbon relative to the benzene ring is favored due to the polarization of the π -electron of CA (Yamada et al., 1985). Hence, TP-1, TP-2, and TP-3 are proposed as 2-hydroxyl-3-chlorophenyl propionic acid, 2-chloro-3-hydroxylphenyl propionic acid, and 1-chloro-2-phenylethylene, respectively (Fig. 7). Brominated analogues of TPs 1-3 were previously detected from HOBr reaction with CA involving the formation of a bromonium ion intermediate (Yamada et al., 1985), the corresponding chloronium ion is likely also formed in the case of HOCl (Fig. 7). HOCl/Cl-adduct products were also reported for chlorination of carbamazepine and CA derivatives (Norwood et al., 1980; Soufan et al., 2013). TP-1 and TP-2 were also detected from the CA (5 μ M) reaction with HOCl (2.4 mM) at pH 7.0 with a similarly higher response of peak TP-2 than TP-1 (Figure S18a, SI). TP-3 was not detected at pH 7.0, while a new peak (TP-4) with m/z of 163.0401 appeared in ESI(-) mode (Figure S18, SI).

4. Conclusion

The kinetics and mechanisms for the reactions of selected aliphatic and aromatic olefins with chlorine and bromine species were investigated. The following conclusions can be drawn:

- HOCl has a low reactivity towards selected olefins with species-specific second-order rate constants $< 1.0 \text{ M}^{-1}\text{s}^{-1}$, nearly 4-6 orders of magnitude lower than for Cl_2O and Cl_2 .
- Cl_2 is non-negligible for chlorination of olefins at lower pH ($pH \leq 6.0$) in the presence of excess Cl^- , while Cl_2O plays an important role near neutral pH ($6.0 < pH \leq 7.5$) at high FAC concentration. Nevertheless, HOCl is the dominant chlorine species for the oxidation of the selected olefins under typical drinking water chlorination conditions.
- HOBr has a large variation of reactivities towards the selected olefins with species-specific second-order rate constants ranging from < 0.01 to $> 10^3 \text{ M}^{-1}\text{s}^{-1}$, about 3-4 orders of magnitude lower than for Br_2O .
- The reactivities of chlorine and bromine species towards olefins increases in the order of $HOCl < HOBr < Br_2O < Cl_2O \approx Cl_2$.
- Electron-donating groups (e.g., CH_2OH - and CH_3 -) enhance the reactivities of cinnamic-type olefins towards chlorine and bromine species by a factor of 3-100, while electron-withdrawing groups (e.g., Cl -, Br -, NO_2 -, $COOH$ -, CHO -, $-COOR$, and CN -) reduce the reactivities by a factor of 3-10000.
- HOCl- and/or Cl - adducts are generated during chlorination of cinnamic acid at pH 5.0 and 7.0.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2020.116424](https://doi.org/10.1016/j.watres.2020.116424).

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