Chlorination and bromination of olefins: Kinetic and mechanistic aspects

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\textbf{A B S T R A C T}

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 (Cl\textsubscript{2}O) and chlorine (Cl\textsubscript{2}) 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\textsuperscript{-1}s\textsuperscript{-1}, about 4-6 orders of magnitude lower than those of Cl\textsubscript{2}O and Cl\textsubscript{2}. HOCl is the dominant chlorine species during chlorination of olefins under typical drinking water conditions, while Cl\textsubscript{2}O and Cl\textsubscript{2} are likely to play important roles at high FAC concentration near circum-neutral pH (for Cl\textsubscript{2}O) or at high Cl\textsubscript{2} concentration under acidic conditions (for Cl\textsubscript{2}). Bromination of the 12 olefins suggests that HOB and Br\textsubscript{2}O are the major reactive species at pH 7.5 with species-specific second-order rate constants of Br\textsubscript{2}O nearly 3-4 orders of magnitude higher than of HOB (ranging from <0.01 to 10\textsuperscript{3} M\textsuperscript{-1}s\textsuperscript{-1}). The reactivities of chlorine and bromine species towards olefins follow the order of HOCl < HOB < Br\textsubscript{2}O < Cl\textsubscript{2}O \approx Cl\textsubscript{2}. Generally, electron-donating groups (e.g., CH\textsubscript{2}OH- and CH\textsubscript{2}−) enhances the reactivities of olefins towards chlorine and bromine species by a factor of 3-10\textsuperscript{2}, while electron-withdrawing groups (e.g., Cl-, Br-, NO\textsubscript{2}-, COOH-, CHO-, -COOR, and CN-) reduce the reactivities by a factor of 3-10\textsuperscript{4}. A reasonable linear free energy relationship (LFER) between the species-specific second-order rate constants of Br\textsubscript{2}O or Cl\textsubscript{2}O reactions with aromatic olefins and their Hammett σ\textsubscript{A} was established with a more negative ρ value for Br\textsubscript{2}O than for Cl\textsubscript{2}O, indicating that Br\textsubscript{2}O is more sensitive to substitution effects. Chlorinated products including HOCl-adducts and decarboxylated Cl\textsubscript{2}O-adducts 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 disinfection by-products (DBPs) or harmful transformation products can be generated from the reactions of oxidants with water matrix compounds 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\textsuperscript{-}) 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\textsuperscript{II}, As\textsuperscript{III}, CN\textsuperscript{-}, and NO\textsubscript{2}\textsuperscript{-}) under water treatment conditions, but not for others such as Mn\textsuperscript{II} (Deborde and von Gunten, 2008; Allard et al., 2013). The reactivity of FAC towards organic compounds is
influenced by their electronic properties with species-specific second-order rate constants varying over a wide range from $< 0.1$ to 10$^6$ M$^{-1}$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; Acreo et al., 2005a; Criotet et al., 2013; Gao et al., 2018), neutral amines (Armento et al., 1993; Antelo et al. 1995; Dodd and Huang, 2004; Dodd et al., 2005), and reduced sulfur moieties (Armento et al., 2000; Pattison and Davies, 2001). Chlorine species is another factor influencing FAC reactivity towards organic compounds. HOCI and OCI$^-$ (Eq. (1), (Morris, 1966)) are often regarded as the main chlorine species during chlorination with HOCI often controlling reaction kinetics (Deborde and von Gunten, 2008).

\[ \text{HOCI} + \text{OCI}^- + \text{H}^+ \rightarrow \text{HOCI} + \text{H}_2\text{O} \quad \text{pK}_1 = 7.5 \quad \text{(Morris, 1966)} \quad (1) \]

However, other chlorine species such as chlorine monoxide (Cl$O$) and chlorine (Cl$_2$) have drawn increasing scientific attention (Sivey et al., 2010; Sivey and Roberts, 2012; Cai et al., 2013; Lau et al., 2016, 2019; Rose et al., 2020). Cl$_2$O is formed via dehydration of 2 HOCI molecules (Eq. (2), 25 °C, 0.0 M ionic strength (Sivey et al., 2010)).

\[ \text{HOCI} + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \quad \text{log K}_3 = 3.36 \quad (2) \]

These chlorine species are often overlooked due to their low concentrations, which are several orders of magnitude lower than HOCI/OCI$^-$. For example, the concentrations of HOCI, OCI$^-$, Cl$_2$O, and Cl$_2$ are around 1.4 × 10$^{-5}$, 1.4 × 10$^{-5}$, 1.7 × 10$^{-12}$, and 2.3 × 10$^{-13}$ M, respectively, at pH 7.5 under typical drinking water chlorination conditions (e.g., FAC = 2.0 mg/L as Cl$_2$ ≈ 28 μM, [Cl$^-]$ = 8 mg/L ≈ 0.23 mM, [Cl$^-]$ 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$_2$O 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 HOCI, Cl$_2$O, and Cl$_2$ with dimethanid were around 0.18, 1.37 × 10$^6$, and 1.21 × 10$^6$ M$^{-1}$s$^{-1}$, respectively, and Cl$_2$O 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 antipyrene (an anti-inflammatory drug) by chlorine increased with decreasing pH with a contribution of >42% at pH < 3.2, while Cl$_2$O 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$_2$O while Cl$_2$O plays an important role at 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 matrices and is highly relevant in oxidation processes (Heeb et al., 2014; Wind, 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).

\[ \text{HOCI} + \text{Br}^- \rightarrow \text{HOBr} + \text{Cl}^- \quad k = 1.6 \times 10^3 \text{M}^{-1}\text{s}^{-1} \quad (4) \]

\[ \text{HOBr} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OBr}^- \quad \text{pK}_5 = 8.8 \quad (5) \]

HOBr shows significant reactivities towards phenols, neutral amines, sulfamides, and sulfur-containing compounds with reactivity generally higher than HOCI 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 ($k_{app} \approx 10^3$-10$^4$ M$^{-1}$s$^{-1}$) are on average about 3000 times higher than for HOCI. 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$_2$O can be formed via dehydration of 2 HOBr molecules (Eq. (6), 25 °C, 0.0 M ionic strength (Sivey et al., 2013)).

\[ 2\text{HOBr} \rightarrow \text{Br}_2\text{O} + \text{H}_2\text{O} \quad \text{log K}_6 = 0.80 \quad (6) \]

Br$_2$ is formed in the presence of excess Br$^-$ under acidic conditions (i.e., [Br$^-]$ > [FAC], Eq. (7), 25 °C, 0.0 M ionic strength (Beckwith et al., 1996)). However, such conditions are unlikely for most drinking waters.

\[ \text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O} \quad \text{log K}_7 = 8.46 \quad (7) \]

Other mixed bromine-chlorine species such as BrCl and BrOCI 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)).

\[ \text{HOBr} + \text{Cl}^- + \text{H}^+ \rightarrow \text{BrCl} + \text{H}_2\text{O} \quad \text{log K}_8 = 3.68 \quad (8) \]

\[ \text{HOBr} + \text{HOCI} = \text{BrOCI} + \text{H}_2\text{O} \quad \text{log K}_9 = -0.46 \quad (9) \]

HOBr controls the speciation of bromine at pH 7.5 for typical drinking water conditions (i.e., [FAC] = 2.0 mg/L as Cl$_2$ ≈ 28 μM, [Cl$^-]$ = 8 mg/L ≈ 0.23 mM, [Br$^-]$ = 100 μg/L ≈ 1.25 μM) with a concentration nearly 5-8 orders of magnitude higher than Br$_2$O, BrOCI, and BrCl (Text S2 and Figure S2a, SI). Br$_2$O may play an important role if excess Br$^-$. [Br$^-]$ is present (e.g., [FAC] = 2.0 mg/L as Cl$_2$ ≈ 28 μM, [Cl$^-]$ = 8 mg/L ≈ 0.23 mM, [Br$^-]$ = 29.25 μM, [Br$^-]$ = [Br$^-]_{total}$ - [FAC] = 1.25 μM ≈ 100 μg/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$_2$O, Br$_2$, BrCl, and BrOCI with dimethanid were up to 10$^3$-10$^6$ times higher than for HOBr. BrCl is predominant at pH < 7.0, while HOBr dominated the overall transformation of dimethanid at pH > 7.0 under typical drinking water chlorination conditions (i.e., [FAC] = 2.0 mg/L as Cl$_2$ ≈ 28 μM, [Cl$^-]$ = 10.5 mg/L ≈ 0.3 μM, [Br$^-]$ = 100 μg/L ≈ 1.25 μM). Contributions of Br$_2$O, BrOCI, and BrCl were <20% in the pH range of 5-9. However, they become increasingly important at higher Cl$^-$(for BrCl), FAC (for BrOCI), or Br$-$ (leading to higher HOBr and consequently higher Br$_2$O concentrations) concentrations. For example, Br$_2$O contributed ~3.5% to dimethanid transformation under typical drinking water chlorination conditions at pH 7.5 in the presence of 1.25 μM Br$-$ (~100 μg/L), while it contributed ~13.1% and 28.4% when the Br$-$ concentration increased to 5.0 μM (~400 μg/L) and 10 μM Br$-$ (~800 μg/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$_2$O, Cl$_2$, Br$_2$, BrCl, and BrOCI) 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
Olefinic compounds. Olefins are electron-rich compounds, which are frequently present in anthropogenic and natural micropollu-
tants such as carbamazepine, ionones, β-cyclodextrin, and micro-
cystsins (Tixier et al., 2003; Nikolau 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 reactiv-
ties, however, generally only limited kinetic information is avail-
able (Staff et al., 2007, 2008). It has been reported that the relative
importance of Cl₂O and Cl₂ increases with decreasing reaction of
the target compound towards HOCl (Sivey et al., 2012). Recently,
Lau et al. (2019) reported that Cl₂ and Cl₂O dominated the clor-
ination kinetics of cyclic olefins (e.g., β-ionone) at high Cl⁻ and
HOCl concentrations, respectively. Even though these studies pro-
vide some insights into the reactivity of FAC and bromine (includ-
ing 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 ap-
parent second-order rate constants was investigated by pH varia-
tions 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, Cl₂O, and Cl₂) and bromine species (mainly HOBr and Br₂O)
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 Ωm/cm) obtained from a Milli-
pore 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 negligi-
able effect on the FAC and bromine concentrations for the rele-
vant 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 (ε =350 M⁻¹ cm⁻¹) (Kumar and Margerum, 1987) every week
(concentration changed ≤ 5.0% within one week).

Stock solutions of bromine were obtained by oxidation of potas-
sium bromide (KBr) solutions with a 1.2 times higher ozone con-
centration (1.0-1.1 mM) at pH 4.0 in 2 mM phosphate buffer to
ensure full oxidation of bromine (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 ele-
vated 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 (ε =332 M⁻¹ 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 tem-
perature (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 ([FAC]₀/olefin]₀ or
[bromine]₀/olefin]₀ ≥ 10) working solutions were introduced into
FAC 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),
KCI (0-20 mM) was also added to acetic acid (10 mM) buffered sol-
lutions at pH 5.0. Thereafter, the solution pH was measured and
re-adjusted (addition of FAC or bromine slightly increased the pH)
by H₂SO₄ (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 thiosul-
fate ([thiosulfate]/[FAC]₀ or [thiosulfate]/[bromine]₀ = 5) for high-
performance liquid chromatography (HPLC) analysis of the olefins.
Control experiments showed that thiosulfate had a negligible im-
pace 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-ÖH
(Fig. 1), a stopped-flow system (Hi-Tech Scientific SF-61DX2) was
used. The change in absorbance of Dien-COOH (λ =255 nm) and
Dien-ÔH (λ =228 nm) was monitored at pH 7.5 (10 mM phosphate
buffer) under pseudo-first order conditions with excess bromine
([bromine]₀/[Dien-COOH] or [bromine]₀/[Dien-ÖH]₀ > 10). The ki-
etic data was analyzed by the software Kinetic Studio 2x, 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 × 3.0 mm, 5 μm particle size) and a
Diode Array Detector (UltiMate 3000) was used for the determina-
tion 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 CI⁻
concentration in the FAC solution was analyzed by ion chromatog-
raphy (IC) (ICS3000, Thermo Scientific) with a limit of quantifica-
tion (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 autosam-
ppler. An Atlantis® T3 C18 column (3.0 × 150 mm, 3 μm particle
size) was used for separation. The mobile phase consisted of wa-
ter 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 per-
formed in both positive and negative electrospray ionization mode
(i.e., ESI(+) and ESI(-)).
2.4. Data modeling

Pseudo-first-order rate constants \(k_{\text{obs}}\) for the reactions of olefins with FAC or bromine were determined from linear regressions of the experimental \(\ln([\text{olefins}]_0/\text{[olefins]})\) vs time data. Second-order rate constants \(k_{\text{app}}\) for the reactions of chlorine species \(\text{HOCl, Cl}_2\text{O, and Cl}_2\) and bromine species \(\text{HOBr, Br}_2\text{O}\) 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).

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

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

where \(k\) represents the second-order rate constant for the reaction of FAC with an olefin; \(k_{\text{obs}}\) 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).

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

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

\(k_{\text{obs}}\) 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. \(k_{\text{obs}}\) increases with increasing \([\text{FAC}_0]\), and the resulting \(n\) values range from 1.0±0.2 (for MAO 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 \(\text{Cl}_2\text{O}\) 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., \([\text{Cl}_2\text{O}] = K_3[\text{HOCl}][\text{Cl}^-][\text{H}^+] \approx K_3[\text{HOCl}]^2[\text{H}^+]\) when [HOCl]≈[Cl\(^-\)]). (Eq. (3)) (Lau et al., 2016). Indeed, ion chromatography analyses showed that [Cl\(^-\)] in the FAC solution were about 1.7 times the [HOCl], and this level of [Cl\(^-\)] ([Cl\(^-\)]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, \(\text{Cl}_2\text{O}\), and \(\text{Cl}_2\). Therefore, \(k_{\text{obs}}\) 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 \(k_{\text{HOCl}}\), \(k_{\text{Cl}_2\text{O}}\), and \(k_{\text{Cl}_2}\) represent the species-specific second-order rate constants (M\(^{-1}\)s\(^{-1}\)) for the reactions of HOCl, \(\text{Cl}_2\text{O}\), and \(\text{Cl}_2\) with olefins, respectively.
3.1.2. Chlorination kinetics of Dien-COOH and CA

Role of Cl₂ for the oxidation of organic compounds. Previous studies show that Cl₂ usually plays an important role at pH < 7.5 in the presence of high Cl⁻ concentrations, while Cl₂O is non-negligible at neutral pH (Sivey et al., 2010, 2012; Lau et al., 2016). Based on literature data, the fractions of HOC (f(HOCl), Eq. (14a)), Cl₂O (f(Cl₂O), Eq. (14b)), and Cl₂ (f(Cl₂), Eq. (14c)) to the transformation of selected target compounds by FAC under our experimental conditions (i.e., [FAC] = 0.1-6.0 mM, [Cl⁻]_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).

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

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

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

Cl₂ contributes <5% at [FAC]₀ of 0.1 mM, while it becomes increasingly important with increasing [FAC]₀ for each compound. f(Cl₂) remains <20% for the majority of the compounds (except for two chlorophenols and one cyclic olefin) at pH 7.5 even at [FAC]₀ of 6.0 mM (the maximum [FAC]₀ used in this study). Even though the contribution of Cl₂ 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, kₘ₁₀ for both Dien-COOH and CA increase linearly with increasing Cl⁻ concentrations. kₘ₁₀ for Dien-COOH in the presence of 10 mM Cl⁻ is almost 40 times higher than the value without addition of Cl⁻ ([Cl⁻]_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), alkene (Lau et al., 2019), and p-xylene (Voudrias et al., 1988a, b), which was attributed to the reaction of Cl₂. Based on Eq. (3), the formation of Cl₂ is favored in the presence of Cl⁻ at lower pH. k₅₅ and k₅₅ for Dien-COOH and CA could be obtained by fitting the experimental data in Fig. 2 (2(a), (2(d), 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 k₅₅ and k₅₅ were (9.9±1.5) × 10⁵ M⁻¹ s⁻¹ and (1.1±0.2) × 10⁶ M⁻¹ s⁻¹ for Dien-COOH; and (2.6±0.8) × 10⁴ M⁻¹ s⁻¹ and (4.2±0.1) × 10⁴ M⁻¹ s⁻¹ for CA, respectively (Table 1).
Overall, Cl₂O and Cl₂ have comparable reactivities towards Dien-COOH and CA (within a factor of 2). The concentrations of HOCI, Cl₂O, and Cl₂ 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), HOCI is by far the dominant chlorine species, followed by Cl₂O with a concentration nearly 35 times higher than that of Cl₂. Therefore, the low calculated concentration of Cl₂ leads to only a small contribution (f(Cl₂) < 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. \( k_{\text{obs}} \) for Dien-COOH and CA showed a strong pH-dependence, with a decreasing trend as the pH increased (Fig. 4). The pH dependence of \( k_{\text{obs}} \) for Dien-COOH and CA was fitted by Eq. (13) with the obtained values for \( k_{\text{HOCI}} \), \( k_{\text{Cl₂O}} \), and \( k_{\text{Cl₂}} \) (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. \( f(\text{HOCI}) \), \( f(\text{Cl₂O}) \), and \( f(\text{Cl₂}) \) for the chlorination of Dien-COOH and CA in the investigated pH range are shown in Figures S8c-S8d (SI). \( f(\text{Cl₂}) \) was ~60% at pH 5 for both Dien-COOH and CA, and decreased to ~5% at pH 7. Cl₂O played an important role at circum-neutral pH with \( f(\text{Cl₂O}) \) ≤20% for both Dien-COOH and CA, while \( f(\text{Cl₂O}) \) decreased significantly at lower and higher pH. \( f(\text{HOCI}) \), \( f(\text{Cl₂O}) \), and \( f(\text{Cl₂}) \) 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 Cl₂ decreased as the pH increased with \( f(\text{Cl₂}) \) decreasing from >30% at pH 5 to <2% at pH 7.5 for both olefins.

Though \( f(\text{Cl₂O}) \) reached the maximum at neutral pH, it was <5% in the pH range investigated. These results suggest that Cl₂ tends to contribute to the chlorination kinetics of olefins in the presence of Cl⁻ at lower pH (pH<6.0), while Cl₂O plays a more significant role in the pH range of 6.0 ≤pH≤7.5 at high FAC concentrations. However, for conditions relevant for drinking water, the contributions of Cl₂ and Cl₂O for the reactions with Dien-COOH and CA are typically low (Figures S8e-S8f, SI).

### Contributions of HOCI and Cl₂O to the oxidation of selected olefins by FAC

**Determination of kinetic parameters.** The above results suggest that Cl₂ contributes only slightly to the chlorination kinetics of olefins at pH >6.0. Therefore, to simplify the modeling process, Eq. (13) was adapted to Eq. (15) by excluding the Cl₂ reactions for pH >6.0.

\[
\text{obs} = k_{\text{HOCI}}[\text{HOCI}] + k_{\text{Cl₂O}}[\text{Cl₂O}]
\]

(15)

Second-order rate constants for the reactions of HOCI (\( k_{\text{HOCI}} \)) and Cl₂O (\( k_{\text{Cl₂O}} \)) with olefins were computed by fitting data of \( k_{\text{obs}} \) (Fig. 2) with nonlinear least-squares regressions based on Eq. (15). The \( k_{\text{obs}} \) data for each olefin at pH 7.5 is well predicted (lines in Fig. 2) and the corresponding values for \( k_{\text{HOCI}} \) and \( k_{\text{Cl₂O}} \) are compiled in Table 1. For each of the selected olefins (except for MCA), \( k_{\text{Cl₂O}} \) was 4-6 orders of magnitude higher than \( k_{\text{HOCI}} \). \( f(\text{Cl₂O}) \) and \( f(\text{HOCI}) \) 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, \( f(\text{Cl₂O}) \) increases gradually with increasing [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 Cl₂O with olefins, as determined with Eq. (15) with data from Fig. 2 and bромine (HOBr) and Br₂ (O) based on Eq. (17) with data from Fig. 2 and bromine (HOBr) and Br₂ (O) based on Eq. (17) with data from Fig. 2 and bromine (HOBr) and Br₂ (O) based on Eq. (17) with data from Fig. 2 and bromine (HOBr) and Br₂ (O) based on Eq. (17) with data from Fig. 2.

![Fig. 5. Calculated fractions of Cl₂O (f(Cl₂O)) to the total extent of chlorination of target compounds as a function of the k_{HOCl}/k_{Cl₂O} 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_{Cl₂O} 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.](image)

f(Cl₂O) was >50% for olefins such as 4-CICA, 4-BrCA, and α-CH₂CA. 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(Cl₂O) and f(HOCl) for the transformation of selected olefins by FAC as well as the half-lives (t₁/₂) 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 Cl₂O 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 Cl₂O plays an equal or more significant role compared to HOCl (Figure 59, SI). This disparity is due to the lower concentration of FAC applied for typical drinking water chlorination conditions (i.e., [FAC] = 2.0 mg/L as Cl₂ ≈ 28 μM), leading to much lower Cl₂O concentrations (Figure S1, SI). Overall, f(Cl₂O) to the transformation of olefins by chlorine is mainly determined by two factors, (i) the relative reactivities of HOCl and Cl₂O towards olefins (k_{HOCl}/k_{Cl₂O}); and (ii) the HOCl concentration (Eq. (16), originating from Eq. (14b) by excluding the negligible contribution of Cl₂).

\[
f(Cl₂O) = \frac{k_{Cl₂O}[Cl₂O]}{k_{Cl₂O}[Cl₂O] + k_{HOCl}[HOCl]} = \frac{k_{Cl₂O}K₂[HOCl]^2}{k_{Cl₂O}K₂[HOCl]^2 + K₁HOCl[HOCl]} = \frac{1}{1 + \frac{K₁}{K₂[HOCl]}} \tag{16}
\]

f(Cl₂O) were calculated as a function of k_{HOCl}/k_{Cl₂O} (10⁻⁸⁻10⁻³) for various FAC concentrations ([FAC] = 0.028-6.0 mM) (Fig. 5). f(Cl₂O) increases with increasing reactivity of Cl₂O (i.e., decreasing k_{HOCl}/k_{Cl₂O}) for each HOCl concentration. A higher f(Cl₂O) can be calculated at higher HOCl concentrations for a fixed k_{HOCl}/k_{Cl₂O}.

The t₁/₂ during chlorination ([FAC] = 2.0 mg/L as Cl₂ ≈ 28 μM) of the selected olefins varies from ~40 min (for Dien-OH) to >126 days (for 4-NO₂CA) with values ≥11 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([olefins]/[olefins]₀) obtained under pseudo-first-order conditions (i.e., [bromine]₀/[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. kₐₒₜ for bromine reactions with olefins (3 μM) increases with increasing initial bromine concentrations ([HOBr]₀, 0.03-0.85 mM) at pH 7.5 (Fig. 6). The corresponding reaction order in bromine was obtained by plotting log(kₐₒₜ) vs log ([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 > 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 [HOBr]² (Eq. (6)). Accordingly, the observed first-order rate constants for the reactions of bromine with olefins can be interpreted by Eq. (17):

\[
k_{\text{obs}} = k_{\text{HOBr}}[\text{HOBr}] + k_{\text{Br}_2\text{O}}[\text{Br}_2\text{O}]
\]

(17)

k_{\text{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_{\text{HOBr}} and k_{\text{Br}_2\text{O}} values were obtained by fitting k_{\text{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_{\text{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_{\text{HOBr}} (n < 0.01- > 10² M⁻¹ s⁻¹). The fractions of HOBr (f(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 [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_Cl₂O for Dien-COOH (9.9 × 10³ M⁻¹ s⁻¹), 4-BrCA (2.0 × 10⁴ M⁻¹ s⁻¹), and α -CH₃CA (1.4 × 10⁵ M⁻¹ s⁻¹) are much higher than k_Br₂O, i.e., 2.5 × 10⁵ M⁻¹ s⁻¹ for Dien-COOH, 4.0 × 10⁵ M⁻¹ s⁻¹ for 4-BrCA, and 9.4 × 10⁵ M⁻¹ s⁻¹ for α -CH₃CA, respectively. In comparison, HOBr is more reactive towards selected olefins than HOCI (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 dimethanediol following the order of HOCI < HOBr < Br₂O < Cl₂O ≈ Cl₂ < BrOCI ≈ Br₂ < BrCl, which was explained by the differences in nucleofugality and polarizability of these halogen species (Sivey et al., 2013). Though BrOCI, 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 substrates on the kinetics of the reactions of FAC and bromine with olefins and linear free energy relationship (LFER)

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

Aliphatic olefins. The species-specific second-order rate constants in Table 1 demonstrate that substrates 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±0.1) × 10³ M⁻¹ s⁻¹) > Dien-COOH ((9.9±1.5) × 10⁵ M⁻¹ s⁻¹) > Dien-CHO ((6.8±0.9) × 10⁵ M⁻¹ s⁻¹). A similar trend was observed for k_HOCI with Dien-OH (19.0±1.5 M⁻¹ s⁻¹) > Dien-COOH (4.0±0.6 M⁻¹ s⁻¹) > Dien-CHO (0.1±0.01 M⁻¹ 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 HOCI (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 10²), 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 (σ* = 2.15 and -0.06 for -CHO and -COO⁻, respectively (Lee and von Gunten, 2012)).

Aromatic olefins. For aromatic olefins including CA and its derivatives, substrates at both the benzene ring and at the olefin bond were investigated (Fig. 1 and Table 1). Furthermore, a cinematic acid methyl ester was investigated. HOCI shows very low reactivities towards CA and its derivatives with k_HOCI < 1.0 M⁻¹ s⁻¹, whereas the substrate effects are mainly discussed based on olefin reactions with Cl₂O. k_Cl₂O for CA derivatives (with substituents at the benzene ring) decrease in the order of 4-CH₃CA ≈ 2-CH₃CA > CA ≈ 4-CICA ≈ 4-BrCA >> 4-NO₂CA. The methyl group as an electron-donor (i.e., Hammet 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_HOCI 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 constant rate 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 Hammet 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_Cl₂O for the reaction of α -CH₃CA with Cl₂O was 10 times higher compared to CA, while k_Cl₂O for the reaction of 4-Cl-α-CNCA with Cl₂O was nearly 10 times lower compared to 4-CICA (Table 1).
These observations can be explained by the electron-donating effect of the methyl group in $\alpha$-CH$_2$CA, which increases the electron density of the double bond. In contrast, the cyano group in 4-Cl-$\alpha$-CNCA reduced the electron density of the double bond due to its electron-withdrawing character (Lee and von Gunten, 2012). For MCA, Cl$_2$O 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$_2$-) 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 10-100000) (Table 1).

### 3.3.3. LFER

A LFER for the reactions of CA and its derivatives with Cl$_2$O/Br$_2$O was developed. A previous study showed that Taft constants $\sigma^+$ were the most suitable descriptors for establishing LFER relationships for olefin reactions with ozone (Lee and von Gunten, 2012). An attempt was made to establish a relationship between $k_{Cl, O}$ or $k_{Br, O}$ for selected olefins vs Taft $\sigma^+$ but it was impossible due to the lack of Taft $\sigma^+$ for most of the substituents on the olefins. In contrast, a reasonable correlation between log ($k_{Cl, O}$) or log ($k_{Br, O}$) and Hammett $\sigma^+$ for the reaction of Cl$_2$O or Br$_2$O with CA derivatives (with substituents at the benzene ring) could be established (Figures S14a-S14b, SI). Negative slopes ($\rho$) were obtained for both cases with $-2.6\pm0.3$ ($R^2 = 0.95$) for Cl$_2$O and $-3.8\pm0.3$ ($R^2 = 0.96$) for Br$_2$O. The more negative $\rho$ value for Br$_2$O than for Cl$_2$O indicates that Br$_2$O is more sensitive to substituent effects. Moreover, the LFER between log ($k_{Cl, O}$) or log ($k_{Br, O}$) vs Hammett $\sigma^+$ by excluding 4-NO$_2$CA was also assessed. Acceptable correlations ($R^2 = 0.76$ and 0.84 for Cl$_2$O and Br$_2$O, respectively, Figures S14c-S14d, SI) were obtained with a similar trend as observed by including 4-NO$_2$CA (Figure S14a-S14b, SI). These results confirm that though 4-NO$_2$CA 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 $\mu$M) with CA (5 $\mu$M) at pH 5.0 were analyzed by HPLC/HRMS in both (ESI (+)) and (ESI (-)) mode. Three transformation products (TPs
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 C₆H₅ClO₂ (M–H–Cl−) based on their fragment ions of 163.0401(C₆H₆O₂, [M–HCl]−) and 119.0503(C₅H₅O, [M–HCl–COO]−) (Figure S16, SI) and their chlorine isotopic patterns (i.e., 35Cl/37Cl =3/1, Figure S17, SI), corresponding to HOCl-adduct products of CA (C₆H₅O₂). 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 C₆H₅Cl, 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-hydroxyphenyl 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 carba-mazepine and CA derivatives (Norwood et al., 1980; Soufan et al., 2013). TP-1 and TP-2 were also detected from the CA (5 μM) 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 M⁻¹s⁻¹, nearly 4-6 orders of magnitude lower than for Cl₂O and Cl₂.
- Cl₂ is non-negligible for chlorination of olefins at lower pH (pH ≤6.0) in the presence of excess Cl⁻, while Cl₂O plays an important role near neutral pH (6.0 <pH ≤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 >10³ M⁻¹s⁻¹, about 3-4 orders of magnitude lower than for Br₂O.
- The reactivities of chlorine and bromine species towards olefins increases in the order of HOCl < HOBr < Br₂O < Cl₂O ≈ Cl₂.
- Electron-donating groups (e.g., CH₂OH- and CH₃-) 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-, NO₂-, 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

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