

Aqueous Chlorination Kinetics of Cyclic Alkenes—Is HOCl the Only Chlorinating Agent that Matters?

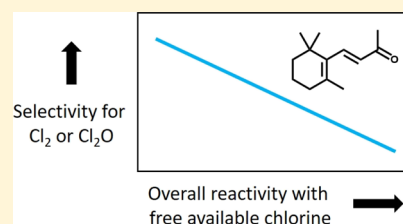
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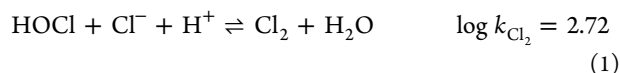
Supporting Information

ABSTRACT: Although Cl_2 and Cl_2O have been recognized as highly reactive constituents of free available chlorine (FAC), robust rate constants for Cl_2 and Cl_2O remain scarce in the environmental literature. In this work, we explored the chlorination kinetics of three structurally related alkenes (α -ionone, β -ionone, and dehydro- β -ionone), a class of compounds whose reactivities with Cl_2 and Cl_2O have not been previously investigated. Second-order rate constants for Cl_2 , Cl_2O , and HOCl were computed from experimental rate constants obtained at various pH values, $[\text{Cl}^-]$, and $[\text{FAC}]$. Our results show that while HOCl is the predominant chlorinating agent for the most reactive alkene, Cl_2 and Cl_2O can dominate the chlorination kinetics of the less reactive alkenes at high $[\text{Cl}^-]$ and high $[\text{FAC}]$, respectively. The tradeoff between overall reactivity with FAC and selectivity for Cl_2 and Cl_2O previously observed for aromatic compounds also applies to the alkenes examined. In laboratory experiments in which high $[\text{FAC}]$ may be used, omission of Cl_2O in data modeling could yield second-order rate constants of dubious validity. In chlorinating real waters with elevated $[\text{Cl}^-]$, formation of Cl_2 may enhance the formation kinetics of chlorinated disinfection byproducts (DBPs) and exacerbate the burden of DBP control for water utilities.



INTRODUCTION

Despite advances in water disinfection technology over the past decades, aqueous chlorine (also known as free available chlorine, or FAC) remains the most commonly used disinfectant for drinking water treatment in the United States and Canada.¹ FAC is known to form potentially toxic disinfection byproducts (DBPs) upon reactions with organic compounds,² and HOCl ($\text{pK}_a = 7.54$ at 25 °C, ref 3) is often regarded as the predominant chlorinating agent in FAC under typical drinking water treatment conditions. Over the past several years, however, studies have emerged to show that molecular chlorine (Cl_2) and dichlorine monoxide (Cl_2O), which are minor constituents of FAC, can also influence the chlorination kinetics of some organic compounds. Cl_2 and Cl_2O exist in equilibrium with HOCl (eqs 1 and 2)



(ref 4, 25 °C, corrected to 0 M ionic strength using the Davies equation)



(ref 5, corrected to 25 °C according to ref 6)

Cl_2 and Cl_2O have been shown to play important roles in the chlorination of aromatic compounds including dimethenamid,⁶ 3-methylanisole,⁷ 1,3-dimethoxybenzene,⁷ and (chloro)-phenols.⁸ Reactivities of FAC with heterocyclic nitrogen compounds such as antipyrine⁹ and aminopyrine¹⁰ similarly cannot be explained unless Cl_2 and Cl_2O are considered.

Whether these chlorinating agents are important for compounds that lack aromatic moieties has not been investigated. Alkenes are particularly underexamined in the aqueous chlorination literature, with apparent rate constants (k_{app}) for reactions with HOCl reported for fewer than five compounds.¹¹ To our knowledge, no second-order rate constants for the reactions of alkenes with Cl_2 and Cl_2O are available. To redress this knowledge gap, we chose to examine the chlorination kinetics of three model alkenes: α -ionone, β -ionone, and dehydro- β -ionone. All three compounds consist of a trimethyl-substituted cyclohexene (or cyclohexadiene) and an α,β -unsaturated ketone (Figure 1). As the number and location of the alkene groups differ in the three ionones, these compounds are anticipated to have different reactivities in the presence of FAC.

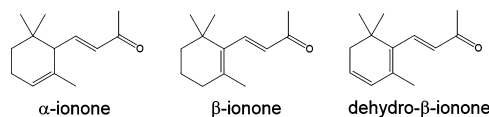


Figure 1. Structures of the alkene-containing compounds investigated in this study.

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Ionones are aroma compounds in flowers¹² and can be found as fragrance ingredients in cosmetics, toiletries, and cleaning products.^{13,14} β -Ionone is particularly important for drinking water treatment because it is also produced by some cyanobacteria^{15,16} and algae^{17,18} via oxidative cleavage of β -carotene,¹⁹ and it can contribute to taste and odor problems in drinking water. Concentrations of β -ionone have been reported to reach as high as 27 ng/L in Lake Zurich, Switzerland¹⁸ and 50 ng/L in Lake Taihu, China²⁰ during algal bloom events. These measured concentrations of β -ionone exceed the compound's odor threshold of 7 ng/L.²¹ To our knowledge, the occurrence of α -ionone and dehydro- β -ionone in natural waters has not been reported. Nonetheless, α -ionone and dehydro- β -ionone serve as useful comparisons for β -ionone because of similarities in the structures of these alkenes.

Ionones are expected to be efficient precursors of trihalo-methanes (THMs) because of their methyl ketone functional groups, known to produce THMs via the haloform reaction.²² Reaction pathways in the presence of FAC have only been investigated for β -ionone; *trans*- β -ionone-5,6-epoxide (or simply β -ionone epoxide) has been hypothesized to be a reaction intermediate that leads to THM formation, whereas β -cyclocitral is proposed to be an intermediate leading to non-THM DBPs.²³ Although the chlorination pathways of α -ionone and dehydro- β -ionone have not been explored, the chlorination mechanisms of other alkenes in aqueous solutions^{24–26} suggest that formation of chlorohydrins and nonchlorinated compounds (e.g., epoxides) are likely.

The objective of this work is to investigate the influence of Cl_2 , Cl_2O , and HOCl on the chlorination kinetics of three ionones in order to obtain robust second-order rate constants that describe the reactivities of these model alkenes in the presence of FAC. Solution pH, $[\text{Cl}^-]$, and $[\text{FAC}]$ were systematically varied in kinetic experiments conducted in batch reactors. Second-order rate constants for Cl_2 , Cl_2O , and HOCl computed from experimental rate constants allow us to elucidate the relationship between alkene structure and alkene reactivity in the presence of FAC.

MATERIALS AND METHODS

A complete list of reagents is available in the [Supporting Information](#) (Table S1). Details of dehydro- β -ionone synthesis, as well as the syntheses of hypothesized intermediates/products of β -ionone chlorination, are also described in the [Supporting Information](#).

Kinetic Experiments. Experiments were conducted in batch reactors (40-mL amber glass vials with PTFE-lined plastic caps) kept in the dark inside a stainless-steel constant-temperature water bath set at 25.00 ± 0.01 °C. Reaction solutions (30 mL) consisted of 10 mM of phosphate buffer (pH 5.5–8.5) or carbonate buffer (pH > 8.5) as well as 0.1 M NaNO_3 (to set the ionic strength). In our previous study⁸ that employed an identical reactor setup, we found that the presence of headspace in the reactor did not affect chlorination kinetics, suggesting that partitioning of chlorine species into the headspace was minimal. Furthermore, control experiments conducted in this study at pH 6–7 without FAC addition revealed that the concentrations of ionones did not change appreciably after ≥ 5 h, indicating that volatilization or hydrolysis did not contribute significantly to the loss of these compounds under our reaction conditions.

The pH of reaction solutions was adjusted using small volumes of 1 M HNO_3 or 1 M NaOH , and solution pH did

not vary by more than 0.05 unit throughout the experiments. Commercially available NaOCl stocks were standardized by iodometric titrations according to Standard Methods 4500- Cl_2 B,²⁷ and working solutions of FAC were prepared by diluting the NaOCl stock with Milli-Q water shortly before each experiment. In most experiments, $[\text{FAC}]_0 = 130$ μM . Stock solutions of ionones were prepared by dissolving the neat compounds in methanol; stocks were subsequently diluted with a solution of 20% (v/v) methanol and 80% (v/v) Milli-Q water to generate spiking solutions. Control experiments were carried out at selected pH values to assess the effect of methanol in the spiking solution on β -ionone chlorination kinetics. Except for experiments in which the initial ionone concentration was varied, nominal $[\text{ionone}]_0 = 5$ μM .

At the start of each kinetic experiment, 1.0 mL of the working FAC solution was added to the reactor using a glass pipet. The reactor was capped, shaken vigorously, and returned to the water bath. After waiting for approximately 8 min for temperature equilibration to occur, the reaction was initiated by spiking the reactor with 0.40 mL of ionone solution (390 μM). The final methanol content in the reactor was approximately 0.25% (v/v). The reactor was again capped, shaken vigorously, and returned to the water bath. Aliquots (2.0 mL) of the reaction solution were periodically collected using a 2-mL glass syringe fitted with a stainless-steel needle. The aliquots were transferred to 4-mL amber glass autosampler vials pre-amended with 0.20 mL of 1,3,5-trimethoxybenzene (TMB) dissolved in 50% (v/v) methanol and 50% (v/v) water ($[\text{TMB}]_0/[\text{FAC}]_0 \geq 3.5$). For experiments conducted at pH > 7.5, the TMB quenching solution contained 0.1 M HNO_3 so as to lower the pH of the sample to <7 at the time of quenching. We have previously demonstrated that TMB can serve as an effective quencher for FAC under similar reaction conditions.²⁸ Rate constants for the chlorination of ionones obtained from experiments using TMB as the quencher are not significantly different (at the 95% confidence interval) from those obtained using sodium thiosulfate as the quencher (data not shown). Efforts were made to follow the disappearance of the parent compound for at least three half-lives. Concentrations of TMB and its monochlorinated product, Cl-TMB , were also monitored in selected experiments to ensure that pseudo-first-order conditions ($[\text{FAC}] \approx [\text{FAC}]_0 = \text{constant}$) were maintained throughout the reaction time courses.

In experiments designed to elucidate the influence of varying $[\text{Cl}^-]$ on kinetics of ionone chlorination, sufficient NaCl was added such that $[\text{Cl}^-]_{\text{added}}$ in the reactor = 1, 3, or 10 mM. $[\text{NaNO}_3]$ was adjusted to maintain constant ionic strength (i.e., $[\text{NaCl}] + [\text{NaNO}_3] = 0.1$ M). To investigate the reaction order in $[\text{HOCl}]$, $[\text{FAC}]_0$ was varied (97–320 μM for α -ionone, 85–380 μM for β -ionone, and 94–310 μM for dehydro- β -ionone) at selected pH values while keeping all other reaction conditions constant. The reaction order in $[\text{ionone}]$ was assessed by varying the initial ionone concentration at a fixed $[\text{FAC}]$ at pH 7.0. $[\text{Ionone}]_0$ was varied from 2.5 to 6.8 μM (for β -ionone) or from 2.1 to 6.2 μM (for α -ionone and dehydro- β -ionone). Effects of varying ionic strength and pH buffer concentration were also investigated in separate experiments. After all the samples were collected and quenched, they were analyzed using high-performance liquid chromatography (HPLC) with photodiode array (PDA) detection. The HPLC–PDA method used for quantifying the ionones is described in the [Supporting Information](#).

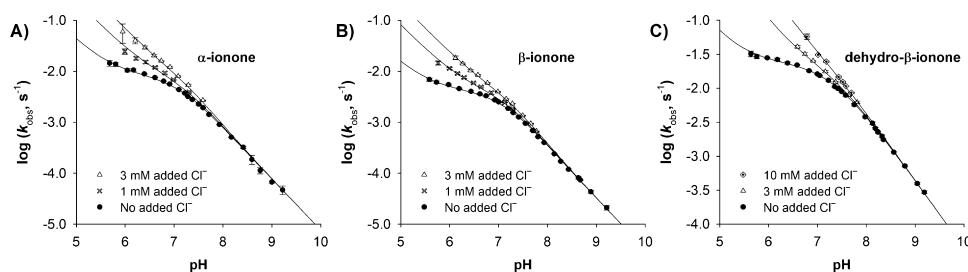


Figure 2. Pseudo-first-order rate constants (k_{obs}) vs pH at varying chloride concentrations for (A) α -ionone, (B) β -ionone, and (C) dehydro- β -ionone. Solid lines are model fits to the form of eq 4. Reaction conditions: $[\text{ionone}]_0 = 5 \mu\text{M}$, $[\text{FAC}]_0 = 130 \mu\text{M}$, $[\text{NaCl}]_{\text{added}} = 0, 1, 3$, or 10 mM , ionic strength (i.e., $[\text{NaCl}]_{\text{added}} + [\text{NaNO}_3] = 0.1 \text{ M}$, [phosphate buffer] (pH 5.5–8.5) or [carbonate buffer] (pH > 8.5) = 10 mM , $T = 25^\circ\text{C}$. Error bars denote 95% confidence intervals (smaller than symbols if not shown).

Identification of Intermediates/Products of β -Ionone Chlorination. In separate experiments, gas chromatography–mass spectrometry (GC–MS), ultra-performance liquid chromatography–quadrupole/time-of-flight MS (UPLC–qTOF–MS), and HPLC–tandem MS (HPLC–MS/MS) were used to detect the intermediates/products of β -ionone chlorination. Details of the chlorination experiments and analytical methods are in the [Supporting Information](#).

Data Modeling. Pseudo-first-order rate constants (k_{obs}) for the loss of ionones were computed from linear regressions of experimental $\ln[\text{ionone}]$ versus time data. Second-order rate constants for Cl_2 , Cl_2O , and HOCl were computed via nonlinear least-squares regressions in SigmaPlot 12.5 (Systat Software). Details of the data modeling process are in the [Supporting Information](#).

RESULTS AND DISCUSSION

Kinetic experiments were conducted under pseudo-first-order conditions in which $[\text{FAC}] \approx [\text{FAC}]_0$ ($\gg [\text{ionone}]_0$) in order to elucidate the roles of Cl_2 , Cl_2O , and HOCl in the aqueous chlorination of three ionones. Pseudo-first-order rate constants (k_{obs}) for the loss of α -ionone, β -ionone, and dehydro- β -ionone were determined from linear regressions of $\ln[\text{ionone}]$ versus time data (example data for β -ionone are shown in [Figure S1](#)). Under our reaction conditions, the overall rate expression for the loss of ionones can be described by eq 3

$$\frac{d[\text{ionone}]}{dt} = -k_{\text{obs}} [\text{ionone}] \quad (3)$$

where k_{obs} is represented by eq 4

$$k_{\text{obs}} = k_{\text{Cl}_2} [\text{Cl}_2] + k_{\text{Cl}_2\text{O}} [\text{Cl}_2\text{O}] + k_{\text{HOCl}} [\text{HOCl}] \quad (4)$$

where k_{Cl_2} , $k_{\text{Cl}_2\text{O}}$, and k_{HOCl} are the second-order rate constants for reactions with Cl_2 , Cl_2O , and HOCl , respectively. Results from our chlorination kinetic experiments are described and discussed in the following sections.

Effects of Varying pH and $[\text{Cl}^-]$. Chlorination experiments were conducted at pH 5.5–9.2 and at various concentrations of added NaCl. The resulting $\log k_{\text{obs}}$ versus pH data for α -ionone, β -ionone, and dehydro- β -ionone are shown in [Figure 2](#). α -Ionone and β -ionone generally reacted with FAC more slowly than did dehydro- β -ionone under similar reaction conditions. Adding 1, 3, or 10 mM of Cl^- while maintaining constant ionic strength led to an increase in k_{obs} at pH ≤ 7 for all three compounds. The increase in k_{obs} with increasing $[\text{Cl}^-]_{\text{added}}$ can be attributed to reactions with Cl_2 , the concentration of which depends on both $[\text{Cl}^-]$ and $[\text{H}^+]$ (eq 1). At pH > 7.5, Cl^- addition did not have any

appreciable effect on k_{obs} , indicating that Cl_2 is not an important chlorinating agent at high pH. Although some previous researchers have suggested that reactions with H_2OCl^+ can cause k_{obs} to increase with decreasing pH,^{29–32} $[\text{H}_2\text{OCl}^+]$ does not depend on $[\text{Cl}^-]$ and thus cannot explain the increase in k_{obs} with added NaCl.

α -Ionone and β -ionone are more sensitive to the effect of Cl^- addition than is dehydro- β -ionone; adding 1 mM of Cl^- to reactors with α - and β -ionones produced a qualitatively similar enhancement in k_{obs} as adding 3 mM of Cl^- to reactors with dehydro- β -ionone. This observation implies that Cl_2 exerts a greater influence on the chlorination kinetics of the less reactive alkenes. For dehydro- β -ionone, a higher concentration (10 mM) of Cl^- was added in order to obtain k_{obs} values that would produce a discernible influence of Cl_2 on the chlorination kinetics of this compound.

The distinction between $[\text{Cl}^-]_{\text{added}}$ and actual $[\text{Cl}^-]$ in the reactor is important because the NaOCl stock solutions used in our experiments contained approximately equimolar concentrations of Cl^- and OCl^- .⁸ The total $[\text{Cl}^-]$ in the reactor was considered in modeling the data from ionone chlorination experiments.

Effects of Varying $[\text{FAC}]$ and $[\text{Ionone}]$. To investigate the reaction order in $[\text{HOCl}]$, $[\text{FAC}]_0$ was varied at selected pH values while maintaining all other reaction conditions constant. The reaction order in $[\text{HOCl}]$ can be represented by eq 5

$$k_{\text{obs}} = k_{\text{app}} ([\text{HOCl}])^n \quad (5)$$

where k_{app} is a pH-dependent apparent rate constant and n is the reaction order in $[\text{HOCl}]$. Taking the log of both sides of eq 5 yields eq 6

$$\log k_{\text{obs}} = \log k_{\text{app}} + n \log [\text{HOCl}] \quad (6)$$

The resulting $\log k_{\text{obs}}$ versus $\log [\text{HOCl}]$ data, as well as the slopes (i.e., n) of the linear regressions, are shown in [Figure S2](#). For α -ionone, the values of n at pH 7.3 and 7.6 without added Cl^- (1.52 ± 0.05 and 1.48 ± 0.07 , respectively) are not significantly different from each other at the 95% confidence level ([Figure S2a](#)). For β -ionone, the largest n (1.71 ± 0.06) was observed at pH 7.0 without added Cl^- , and n decreased with increasing pH ([Figure S2b](#)). When 3 mM of Cl^- was added at pH 7.0, n decreased to 1.43 ± 0.08 . The value of n for dehydro- β -ionone at pH 7.6 without added Cl^- (1.10 ± 0.02) was the lowest observed in our experiments ([Figure S2c](#)).

The influence of Cl_2O on reaction kinetics is anticipated to be most pronounced at high $[\text{HOCl}]$ because $[\text{Cl}_2\text{O}]$ is proportional to $[\text{HOCl}]^2$ (eq 2). Accordingly, a reaction that is

first-order in $[\text{Cl}_2\text{O}]$ will be second-order in $[\text{HOCl}]$. In such a case, plotting $\log k_{\text{obs}}$ versus $\log[\text{HOCl}]$ will yield a slope of 2, with slopes that are between 1 and 2 reflecting contributions from both Cl_2O and HOCl . Complications arise when FAC solutions contain approximately equimolar concentrations of Cl^- and HOCl ; a first-order dependence on $[\text{Cl}_2]$ can masquerade as a second-order dependence on $[\text{HOCl}]$ because $[\text{Cl}_2] = k_{\text{Cl}_2}[\text{H}^+][\text{HOCl}][\text{Cl}^-] \approx k_{\text{Cl}_2}[\text{H}^+][\text{HOCl}]^2$ when $[\text{HOCl}] \approx [\text{Cl}^-]$ (eq 1). We have previously shown that both Cl_2 and Cl_2O must be considered in order to explain the $\log k_{\text{obs}}$ versus $\log[\text{HOCl}]$ data for (chloro)phenols at low pH.⁸ In this study, however, the experiments with varying $[\text{FAC}]$ were conducted at pH 7–8, and $[\text{Cl}^-]_{\text{tot}}$ in the reactor was ≤ 0.5 mM in the absence of added Cl^- . Under these conditions, the influence of Cl_2 should be minor relative to that of Cl_2O . Nonetheless, the increase in $[\text{Cl}^-]$ that would accompany the increase in $[\text{HOCl}]$ was taken into account in modeling the experimental data.

The initial concentration of each ionone was varied to determine the reaction order in $[\text{ionone}]$. Plots of $\log(\text{rate})$ versus $\log[\text{ionone}]_0$ for all compounds are linear with slopes close to 1.0 (Figure S3), indicating that reactions with FAC are first-order in $[\text{ionone}]$.

Effects of Other Solutes. The effect of ionic strength on chlorination kinetics was assessed by varying $[\text{NaNO}_3]$. We found that varying $[\text{NaNO}_3]$ had no appreciable effect on k_{obs} for α - and β -ionones (Figure S4a,b, respectively). There is some scatter in the k_{obs} versus $[\text{NaNO}_3]$ data for dehydro- β -ionone (Figure S4c), but the scatter is likely because of variations in pH across the four reactors.

Some fluctuation exists in the k_{obs} versus $[\text{phosphate}]_{\text{tot}}$ data for α -ionone (Figure S5a), but the effect appears to be modest at $[\text{phosphate}]_{\text{tot}} \leq 10$ mM. As the concentration of pH buffer used in most experiments did not exceed 10 mM, we did not pursue the effect of phosphate buffer on α -ionone chlorination rates further. Phosphate buffer did not affect k_{obs} for β -ionone (Figure S5b) and dehydro- β -ionone (Figure S5c).

Carbonate buffer did not affect k_{obs} for β -ionone (Figure S6a) or dehydro- β -ionone (Figure S6b), although it enhanced k_{obs} for α -ionone (Figure S7). For α -ionone, the degree to which carbonate buffer enhanced k_{obs} at pH 8.6–9.2 decreased slightly with increasing pH. As $\text{p}K_{\text{a}2}$ of the carbonate buffer system is 10.31,³³ our results suggest that bicarbonate (HCO_3^-) has greater catalytic activity than does carbonate (CO_3^{2-}) in the chlorination of α -ionone. Little information is available in the literature on the mechanism by which (bi)carbonate acts as a catalyst in the aqueous chlorination of organic compounds; however, bicarbonate and carbonate ions have been reported to catalyze reactions involving drinking water disinfectants such as the transformation of monobromamine (NH_2Br) to dibromamine (NHBr_2).³⁴ At each pH, we extrapolated the k_{obs} of α -ionone to $[\text{carbonate}]_{\text{tot}} = 0$ using linear regressions of the k_{obs} versus $[\text{carbonate}]_{\text{tot}}$ data; the extrapolated k_{obs} values are the ones shown in Figure 2a.

The final methanol content in each reactor [0.25% (v/v)] was sufficiently low that it should have precluded a cosolvent effect on the activity coefficients of ionones in aqueous solutions.³⁵ Nevertheless, at pH 5.6, the k_{obs} for β -ionone chlorination obtained when β -ionone was added from a methanolic spiking solution was smaller than the one obtained when β -ionone was added from an aqueous spiking solution

(Figure S8a). At pH 7.4, there was no significant difference between the k_{obs} obtained with a methanolic spiking solution and that obtained with an aqueous spiking solution (Figure S8b). As the mixing of reagents should have been completed before the first sample was collected in both sets of experiments, it is not clear why there was a difference in k_{obs} at pH 5.6 but not at pH 7.4. At both pH 5.6 and 7.4, the value of extrapolated $[\beta\text{-ionone}]_0$ was lower with the aqueous spiking solution, most likely because of β -ionone being sparingly soluble in water. As a compromise, in all our chlorination experiments we prepared spiking solutions of the ionones in 20% (v/v) methanol and 80% (v/v) water to keep the compounds dissolved while minimizing the potential effect of methanol on reaction kinetics.

Second-Order Rate Constants. Values of k_{Cl_2} , $k_{\text{Cl}_2\text{O}}$, and k_{HOCl} were computed using nonlinear least-squares regressions of the experimental $\log k_{\text{obs}}$ data in SigmaPlot 12.5. A sequential approach to parameter-fitting and second-order rate constant determinations, rather than simultaneously modeling the entire data set using all fitting parameters, was employed because of the reduced likelihood of producing an over-parameterized model. As detailed in the Supporting Information, the $\log k_{\text{obs}}$ vs pH data were grouped such that the contribution of a particular chlorinating agent toward k_{obs} would be most significant in that data group. Figure 2 shows that a model of the form of eq 4 fits the data well at all values of $[\text{Cl}^-]_{\text{added}}$. We found that we did not need to include a term for H_2OCl^+ in order for our model to fit the data.

Best-fit estimates of k_{Cl_2} , $k_{\text{Cl}_2\text{O}}$, and k_{HOCl} are shown in Table 1. The overall reactivity of ionones with FAC increases from β -

Table 1. Second-Order Rate Constants for the Chlorination of Ionones^a

	k_{Cl_2} ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{Cl}_2\text{O}}$ ($\text{M}^{-1} \text{s}^{-1}$)	k_{HOCl} ($\text{M}^{-1} \text{s}^{-1}$)
α -ionone	1.88 (± 0.30) $\times 10^8$	3.26 (± 0.23) $\times 10^7$	28.1 (± 1.0)
β -ionone	6.25 (± 0.45) $\times 10^7$	1.94 (± 0.13) $\times 10^7$	12.0 (± 0.4)
dehydro- β -ionone	2.65 (± 0.44) $\times 10^8$	2.33 (± 0.60) $\times 10^7$	165 (± 3)

^aUncertainties represent 95% confidence intervals.

ionone to α -ionone to dehydro- β -ionone. For all three compounds, k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$ are 5–6 orders of magnitude larger than k_{HOCl} . As the most reactive of the compounds examined, dehydro- β -ionone has the largest values of k_{HOCl} and k_{Cl_2} . The least reactive compound, β -ionone, has the smallest k_{HOCl} and k_{Cl_2} . α -Ionone has the largest $k_{\text{Cl}_2\text{O}}$, but the values of $k_{\text{Cl}_2\text{O}}$ for all three ionones are similar when the uncertainties (reported as 95% confidence intervals) are considered.

The high reactivity of dehydro- β -ionone relative to α - and β -ionones can be rationalized by the differences in their structures. Dehydro- β -ionone has two alkenes that are conjugated in a cyclohexadiene. Assuming that the mechanism of ionone chlorination is electrophilic addition of chlorine to a cyclic alkene, the carbocation that would form upon chlorine addition may be stabilized by the remaining cyclic alkene in dehydro- β -ionone through resonance (Figure S9). This form of resonance stabilization is not possible in α - and β -ionones.

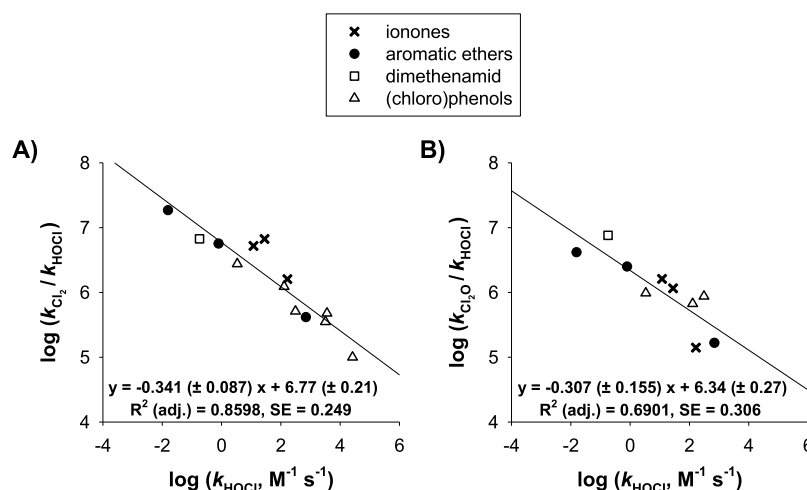


Figure 3. Selectivity versus reactivity for (A) Cl_2 and (B) Cl_2O . Second-order rate constants were obtained from this study as well as those from refs.^{6,8} For (chloro)phenols, only rate constants for the conjugate base forms are included. Uncertainties in the equations denote 95% confidence intervals. SE = standard errors of the regressions.

For dehydro- β -ionone, the presence of a second cyclic alkene in a conjugated system leads to a pronounced enhancement in k_{HOCl} while having a modest (if any) effect on k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$. Variations in the extent to which the second cyclic alkene affects the values of k_{HOCl} , k_{Cl_2} , and $k_{\text{Cl}_2\text{O}}$ may be attributable to the difference in electrophilicity of the chlorinating agents. Cl_2 is more electrophilic than is HOCl because Cl^- (from Cl_2) is a better leaving group than is OH^- (from HOCl). If Cl_2O were to react by a heterolytic mechanism, it would also have a better leaving group (i.e., OCl^-) than does HOCl . The resonance stabilization that is available in the carbocation formed from dehydro- β -ionone is perhaps more important for HOCl , the weakest electrophile, than for Cl_2 and Cl_2O .

β -Ionone is generally less reactive than is α -ionone in the presence of FAC. One possible reason for the lower reactivity of β -ionone with FAC is that the cyclohexene in β -ionone is conjugated with the α,β -unsaturated ketone (also called an enone). As a result, the electron density at the endocyclic alkene in β -ionone is delocalized, and the nucleophilicity of this alkene is lowered. Because the electron density at the endocyclic alkene in α -ionone is not delocalized in a conjugated system, this alkene is anticipated to be more nucleophilic than is the one in β -ionone. Moreover, the trisubstituted alkene in α -ionone is less sterically hindered than the tetrasubstituted alkene in β -ionone, facilitating the approach of electrophiles. Having an alkene that is not part of a conjugated system in a less sterically hindered position could explain the high chlorination rates of α -ionone compared with β -ionone.

Comparisons with Previous Results. There are very limited data on the kinetics of ionone chlorination. Zhang et al.³⁶ reported a pseudo-first-order rate constant of $1.86 \pm 0.12 \text{ min}^{-1}$ (equivalent to $0.031 \pm 0.002 \text{ s}^{-1}$) for the loss of β -ionone at pH 7 and 25 °C when $[\text{FAC}]$ was in large excess of $[\text{ionone}]$ ($[\text{FAC}]_0 = 100 \text{ mg/L}$ as $\text{Cl}_2 \approx 1.41 \text{ mM}$, $[\beta\text{-ionone}]_0 = 20 \text{ mg/L} \approx 104 \text{ }\mu\text{M}$). Using the second-order rate constants for β -ionone listed in Table 1, we predicted a pseudo-first-order rate constant (k_{calc}) of 0.174 s^{-1} at pH 7 (assuming that $[\text{Cl}^-] = [\text{FAC}]_0 = 1.41 \text{ mM}$). Our k_{calc} is more than five times larger than the experimental rate constant determined by

Zhang et al.; the reason for this discrepancy is unclear. Zhang et al.³⁶ also reported a “pseudo-second-order” rate constant of $3.39 \times 10^{-4} \pm 3.85 \times 10^{-5} \text{ L }\mu\text{g}^{-1} \text{ min}^{-1}$ (equivalent to $1.09 (\pm 0.12) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) for the chlorination of β -ionone, but the meaning of this “pseudo-second-order” rate constant is uncertain.

Using values of k_{Cl_2} , $k_{\text{Cl}_2\text{O}}$, and k_{HOCl} for the three ionones obtained in this work as well as those for dimethenamid,⁶ aromatic ethers,⁷ and (chloro)phenols⁸ (obtained under reaction conditions similar to those used in this study and listed in Table S2), we constructed log–log plots of $(k_{\text{Cl}_2}/k_{\text{HOCl}})$ versus k_{HOCl} and $(k_{\text{Cl}_2\text{O}}/k_{\text{HOCl}})$ versus k_{HOCl} (Figure 3a,b, respectively). For the (chloro)phenols, only second-order rate constants for the conjugate base (ArO^-) forms are included because a complete set of rate constants for the acid (ArOH) forms is not available. Even though estimates of k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$ for *p*-xylene are available, the reaction of *p*-xylene with HOCl was sufficiently slow as to preclude estimation of k_{HOCl} .³⁷ Values of k_{Cl_2} , $k_{\text{Cl}_2\text{O}}$, and k_{HOCl} have been reported by Cai et al.^{9,10} for antipyrine and aminopyrine. For antipyrine, the second-order rate constants were fit to the k_{obs} versus pH data at only one set of $[\text{Cl}^-]$ and $[\text{FAC}]$.⁹ For aminopyrine, a different estimate of k_{Cl_2} was reported for each of the $[\text{Cl}^-]_{\text{added}}$ used in kinetic experiments.¹⁰ As the data modeling procedures employed in these studies entail questionable assumptions, the second-order rate constants reported for antipyrine and aminopyrine were excluded from our analysis.

Values of k_{HOCl} are a measure of a compound's intrinsic reactivity in the presence of FAC as HOCl is the most abundant chlorinating agent under conditions relevant to drinking water treatment. Values of $(k_{\text{Cl}_2}/k_{\text{HOCl}})$ and $(k_{\text{Cl}_2\text{O}}/k_{\text{HOCl}})$ reflect the degree to which an organic compound will selectively react with Cl_2 and Cl_2O , respectively, rather than with HOCl . If a compound does not discriminate between HOCl and the other chlorinating agents present in FAC, then we would expect its k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$ values to be equal to its k_{HOCl} (i.e., $k_{\text{Cl}_2}/k_{\text{HOCl}} = 1$ and $k_{\text{Cl}_2\text{O}}/k_{\text{HOCl}} = 1$, both denoting an absence of selectivity). If a compound is more inherently reactive toward Cl_2 and Cl_2O than HOCl , then we would

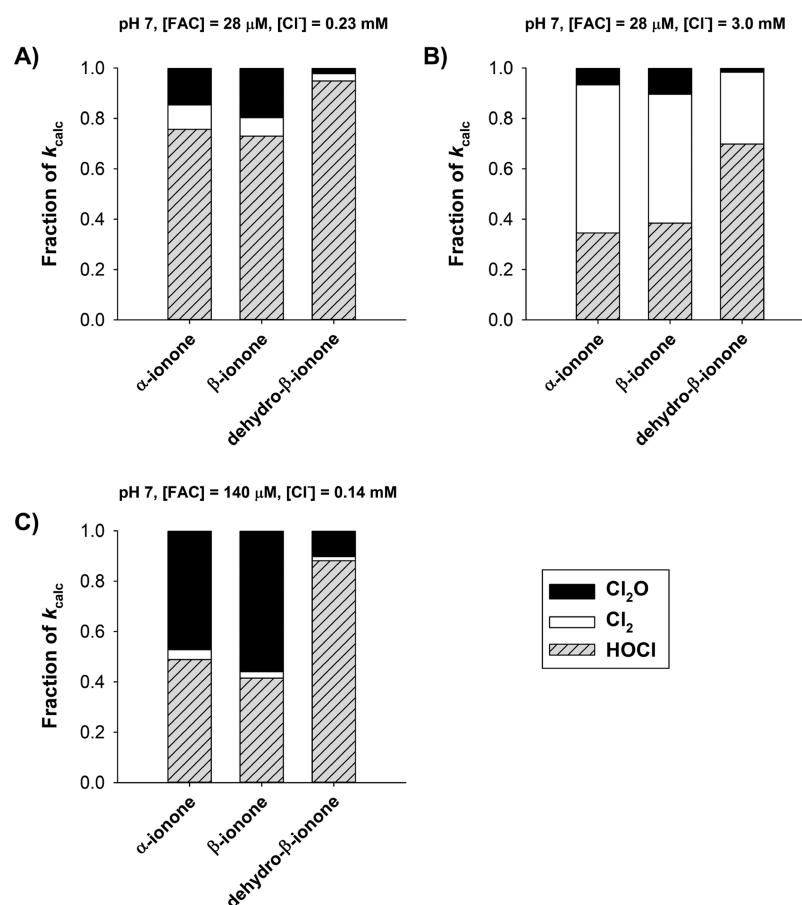


Figure 4. Contributions of Cl_2 , Cl_2O , and HOCl toward k_{calc} under typical conditions for (A) drinking water treatment, (B) chlorination of water with high $[\text{Cl}^-]$, and (C) bench-scale chlorination experiments (see Table S3 for details on the $[\text{FAC}]$ and $[\text{Cl}^-]$ values used to construct this figure; $T = 25^\circ\text{C}$).

expect its k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$ to be greater than its k_{HOCl} (i.e., $k_{\text{Cl}_2}/k_{\text{HOCl}} > 1$ and $k_{\text{Cl}_2\text{O}}/k_{\text{HOCl}} > 1$). As a compound's selectivity for Cl_2 and Cl_2O relative to HOCl increases, the values of $(k_{\text{Cl}_2}/k_{\text{HOCl}})$ and $(k_{\text{Cl}_2\text{O}}/k_{\text{HOCl}})$ would also increase.

Linear regression of $\log(k_{\text{Cl}_2}/k_{\text{HOCl}})$ versus $\log k_{\text{HOCl}}$ yields a slope of -0.341 ± 0.087 (uncertainty represents 95% confidence intervals; Figure 3a). Linear regression of $\log(k_{\text{Cl}_2\text{O}}/k_{\text{HOCl}})$ versus $\log k_{\text{HOCl}}$ yields a slope of -0.307 ± 0.155 (Figure 3b). As the reactivity of a compound increases, selectivity for Cl_2 (Figure 3a) and Cl_2O (Figure 3b) decreases. The correlations shown in Figure 3 are consistent with the reactivity/selectivity principle in physical organic chemistry,³⁸ although it is important to note that many exceptions to this reactivity/selectivity paradigm have been reported.³⁹ There is more scatter in the selectivity versus reactivity plot for Cl_2O than in the one for Cl_2 , most likely because of the large uncertainties associated with some of the $k_{\text{Cl}_2\text{O}}$ values (Table S2).

In our previous study on the chlorination kinetics of six (chloro)phenols, results from our linear free energy relationship correlations indicate that Cl_2O , unlike HOCl and Cl_2 , may not react with organic compounds via electrophilic aromatic substitution.⁸ Nonetheless, although there is uncertainty surrounding the reaction mechanism of Cl_2O with organic compounds, experimental conditions that favored reactions with Cl_2O did not lead to reaction intermediates/products that

were different from those formed under conditions that favored reactions with HOCl and Cl_2 for chlorination of dimethenamid,⁶ three aromatic ethers,⁷ or (chloro)phenols.⁸ Assuming that trends in electrophilic addition of chlorine to alkenes are similar to those in electrophilic aromatic substitutions, HOCl , Cl_2 , and Cl_2O are not anticipated to lead to different transformation pathways for the three ionones.

Caution is advised when using the equations in Figure 3 and k_{HOCl} values reported in the literature to predict k_{Cl_2} and $k_{\text{Cl}_2\text{O}}$. For instance, the reactivity of 2,4,6-trichlorophenol with Cl_2 and Cl_2O may have been misattributed to reactivity with HOCl , thus leading to overestimation of k_{HOCl} for this compound.⁸ Conducting experiments in which pH, $[\text{Cl}^-]$, and $[\text{FAC}]_0$ are systematically varied is necessary for obtaining precise estimates of k_{Cl_2} , $k_{\text{Cl}_2\text{O}}$, and k_{HOCl} .

Pathway of Ionone Chlorination. While we only quantified the parent compounds in our kinetic experiments, some reaction intermediates/products were detected using HPLC–PDA. In the β -ionone chlorination experiments, the presence of an unknown compound was observed in nearly all samples. The increase in peak area of this unknown compound was concurrent with the decrease in $[\beta\text{-ionone}]$ (Figure S1), suggesting that the unknown compound could be an intermediate or a product of β -ionone chlorination. We synthesized several compounds that could potentially be reaction intermediates/products of β -ionone; these compounds were characterized using GC–MS, UPLC–qTOF–MS,

and HPLC–MS/MS. Results and discussion of product characterization are in the [Supporting Information](#).

Practical Implications. Using the second-order rate constants listed in [Table 1](#), we computed the pseudo-first-order rate constants (k_{calc}) at different values of [FAC] and $[\text{Cl}^-]$ that may be encountered in various chlorination scenarios: drinking water treatment ($[\text{FAC}] = 28 \mu\text{M} \approx 2.0 \text{ mg/L}$ as Cl_2 ; $[\text{Cl}^-] = 0.23 \text{ mM} \approx 8 \text{ mg/L}$), disinfection of desalinated water ($[\text{FAC}] = 28 \mu\text{M} \approx 2.0 \text{ mg/L}$ as Cl_2 ; $[\text{Cl}^-] = 3.0 \text{ mM} \approx 110 \text{ mg/L}$), and chlorination experiments conducted in the laboratory ($[\text{FAC}] = 140 \mu\text{M} \approx 9.9 \text{ mg/L}$ as Cl_2 ; $[\text{Cl}^-] = 0.14 \text{ mM} \approx 5.0 \text{ mg/L}$). Further descriptions of the [FAC] and $[\text{Cl}^-]$ values we chose can be found in [Table S3](#). Fractional contributions of various chlorine species toward the overall k_{calc} can then be computed, and the results are presented in [Figures S22–S24](#).

For α -ionone, HOCl is the most important chlorinating agent at pH 6–8 and at a set of [FAC] and $[\text{Cl}^-]$ representative of drinking water treatment ([Figure S22a](#)). When chlorinating water containing higher $[\text{Cl}^-]$ (e.g., desalinated water or freshwater that has been coagulated using FeCl_3), the influence of Cl_2 at pH 6–8 increases substantially ([Figure S22b](#)). In laboratory studies in which the chlorine doses used are often higher than those employed in typical drinking water treatment, the influence of Cl_2O at pH 7–8 becomes pronounced, whereas the influence of HOCl is diminished ([Figure S22c](#)).

The contributions of various chlorinating agents toward the overall reactivity for β -ionone are similar to those for α -ionone. HOCl is the most important chlorinating agent for α -ionone under typical drinking water treatment conditions ([Figure S23a](#)), although the influence of Cl_2 will be significant in the presence of high $[\text{Cl}^-]$ ([Figure S23b](#)). The influence of Cl_2O is most apparent in laboratory experiments employing high [FAC] ([Figure S23c](#)).

The results for dehydro- β -ionone are somewhat different from those for the other two compounds. The role of Cl_2O is insignificant in all the chlorination scenarios considered ([Figure S24](#)), whereas Cl_2 can still exert a substantial influence on dehydro- β -ionone kinetics at high $[\text{Cl}^-]$ at pH 6–7 ([Figure S24b](#)). HOCl contributes the major fraction toward k_{calc} in all scenarios.

In summary, the influence of Cl_2 and Cl_2O on chlorination kinetics is more apparent for α - and β -ionones than for dehydro- β -ionone. At a set of pH, [FAC], and $[\text{Cl}^-]$ representative of drinking water treatment, reactions with Cl_2 and Cl_2O account for <30% of k_{calc} for α - and β -ionones and <10% of k_{calc} for dehydro- β -ionone ([Figure 4a](#)). When water with elevated $[\text{Cl}^-]$ is chlorinated at pH 7, reactions with Cl_2 can contribute nearly 50% toward k_{calc} for α - and β -ionones and close to 30% toward k_{calc} for dehydro- β -ionone ([Figure 4b](#)). In laboratory settings where high chlorine doses may be used, reactions with Cl_2O can account for at least 50% of the reactivities of α - and β -ionones ([Figure 4c](#)). Furthermore, the most reactive of the three ionones (dehydro- β -ionone) is the least selective and will tend to react with the most abundant chlorine species present (i.e., HOCl). The less reactive ionones (α - and β -ionones) will be more selective and thus are more likely to react with Cl_2 and Cl_2O .

The tradeoff between reactivity and selectivity is noteworthy because natural organic matter (NOM) can be divided into fast-reacting and slow-reacting fractions.⁴⁰ The majority of THM precursors in NOM are moderately reactive, and their

reactions with FAC occur on the order of hours to days (rather than seconds to minutes). Findings from this work, as well as those from previous studies,^{7,8} suggest that Cl_2 and possibly Cl_2O may be more important for the slow-reacting fraction of NOM. Furthermore, algal organic matter, of which β -ionone is a component, can also produce THMs upon chlorination.⁴¹ Laboratory studies have shown that both algal cells and algal extracellular products can continue to form THMs after more than 48 h.^{42,43} The moderate reactivities of DBP precursors in algal organic matter may predispose them to reactions with Cl_2 and Cl_2O as well.

In this work, we have shown that Cl^- can enhance the chlorination rates of moderately-reactive organic compounds at pH < 7.5 via the formation of Cl_2 . Other studies have also noted the importance of Cl^- . Addition of chloride at the millimolar level can enhance THM formation from the chlorination of carbohydrates,⁴⁴ and Cl^- can promote the formation of several volatile DBPs in swimming pool water.⁴⁵ Whereas Cl^- concentrations in most surface waters are low, Cl^- levels in many North American rivers and streams are expected to rise because of intensifying urbanization.^{46,47} Moreover, as desalination becomes more widely adopted, the Cl^- concentrations in our drinking water supplies will likely increase. Seawater intrusion because of rising sea levels and overexploitation of coastal groundwaters may also add appreciable amounts of Cl^- to drinking water supplies. Concentrations of Br^- in source waters are also anticipated to increase in the case of desalination and seawater intrusion. Free bromine species tend to be inherently more reactive with organic compounds than are free chlorine species, and it has been shown⁴⁸ that bromine chemistry drives DBP (trans)-formation at high Br^- concentrations. The effect of increasing Cl^- concentrations on overall DBP (trans)formation rates may be eclipsed by the effect of Br^- ; nonetheless, the potential influence of Cl_2 on chlorination kinetics of organic compounds at elevated Cl^- levels should be considered.

In the laboratory, chlorine doses that are higher than those encountered in typical drinking water treatment are often employed to maintain a detectable chlorine residual over hours or days. As a result, Cl_2O formation will be favored in these experimental systems. Researchers sometimes correct for variations in chlorination conditions by dividing the experimental k_{obs} values by [FAC]. We have shown, however, that chlorination reactions will not be first-order in [HOCl] when Cl_2O (and perhaps Cl_2 if FAC solutions are equimolar in $[\text{Cl}^-]$ and [HOCl]) influences the reaction kinetics. Therefore, the validity of normalizing k_{obs} values obtained in laboratory settings in this manner is dubious.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01171.

Additional experimental details, descriptions of analytical methods, kinetic modeling procedure, and other experimental results (PDF)

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Notes

The authors declare no competing financial interest.

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