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Reactions of α,β-Unsaturated Carbonyls with Free Chlorine, Free Bromine, and Combined Chlorine

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Abstract

Chemical disinfection employed in water and wastewater treatment can produce a variety of transformation products, including carbonyl compounds (e.g., saturated and unsaturated aldehydes and ketones). Experiments conducted under conditions relevant to chlorination at drinking water treatment plants and residual chlorine application in distribution systems indicate that saturated carbonyl compounds react slowly with chlorine species, whereas α,β-unsaturated carbonyl compounds readily react with free chlorine and free bromine over a wide pH range. For nearly all of the α,β-unsaturated carbonyl compounds studied, the apparent second-order rate constants for the reaction with free chlorine increased in a linear manner with hypochlorite (OCl^-) concentrations, yielding species-specific second-order rate constants for the reaction with OCl^- ranging from 0.21 to 12 M^{-1} s^{-1}. Predictions based on the second-order rate constants indicate that a substantial fraction of several of the more prominent α,β-unsaturated carbonyls (e.g., acrolein, crotonaldehyde) will be transformed to an appreciable extent in distribution systems by free chlorine. Products from the reaction of chlorine with acrolein, crotonaldehyde, and methyl vinyl ketone were tentatively identified using nuclear magnetic resonance (NMR) and gas chromatography coupled to high resolution time-of-flight mass spectrometry (GC-HRT-MS). These products lacked unsaturated carbons, and in some cases, contained multiple halogens.

Graphical Abstract

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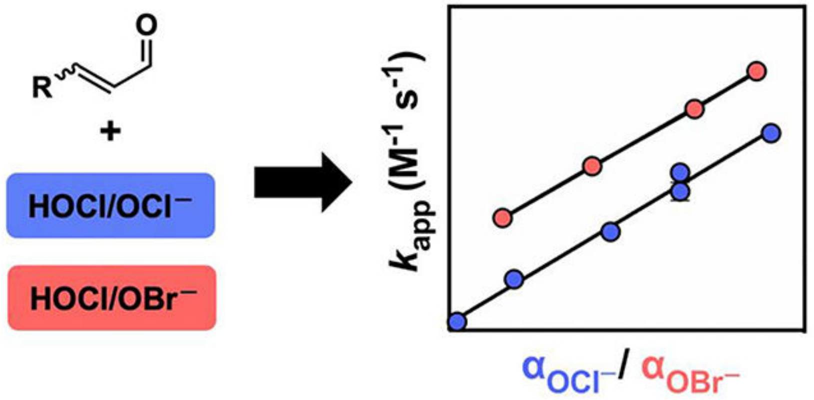

Introduction

Chemical disinfection and oxidative treatment processes (e.g., chlorination, ozonation) are widely employed during drinking water and wastewater treatment.[1] During these processes, oxidation of natural organic matter and synthetic organic compounds by chlorine, ozone, hydroxyl radical ($HO^\bullet$), or sulfate radical ($SO_4^{-\bullet}$) result in the production of transformation products that may be problematic from a toxicological point of view.[1,2]

Efforts to identify compounds responsible for toxicity of treated drinking water have largely focused on halogenated disinfection byproducts.[3] After four decades of research, about 40% of the total organic halogen species and less than 16% of the adsorbable organic halogens (i.e., the fraction determined by solid phase extraction) have been identified.[3–5] Among these compounds, a few (e.g., iodinated acetic acids) have been suggested to be responsible for much of the toxicity measured with *in vitro* bioassays.[6,7]

Due to their size, polarity, and potential volatilization, other classes of compounds (e.g., volatile halogenated byproducts, carbonyl compounds) tend to be lost during the sample concentration methods typically employed prior to *in vitro* bioassays (e.g., solid phase extraction, lyophilization).[4,8,9] As a result, these types of compounds have not been subject to as much scrutiny as other oxidative transformation products. Carbonyl compounds (i.e., aldehydes and ketones) are relatively toxic due to their electrophilicity and their tendency to react with proteins and DNA.[10] In addition to their toxicity, carbonyl compounds can serve as precursors to halogenated disinfection byproducts under certain conditions. For example, ketones react with free chlorine (i.e., $HOCl/OCl^-$) in a multi-step process that results in the formation of halomethanes.[11–13]

Among the carbonyl compounds produced during water treatment, α,β-unsaturated carbonyl compounds have recently received considerable attention due to their relatively high toxicity.[14] These carbonyls are produced when phenolic compounds are treated with UV/H_2O_2 or free chlorine (i.e., $HOCl/OCl^-$).[15,16] α,β-Unsaturated compounds are also produced when benzene and alkylbenzenes react with $HO^\bullet$ or $SO_4^{-\bullet}$.[17] In potable water reuse, α,β-unsaturated aldehydes are formed during ozonation or chlorination of wastewater effluent.[18] Although most of these compounds are removed during biofiltration, in potable reuse systems without biological treatment they can persist during subsequent treatment steps (e.g., reverse osmosis, UV/H_2O_2) that are designed to serve as barriers to chemical contaminants.[19]

Due to their high reactivity, α,β-unsaturated carbonyl compounds might not persist long enough to impact consumers of treated water (i.e., they might be transformed to less toxic compounds within the drinking water distribution system). One potential pathway through which these compounds might degrade involves reactions with free or combined chlorine (i.e., chloramines), which are often used as residual disinfectants. Saturated carbonyls and olefins react slowly with free chlorine,[20–23] either through substitution at the carbon adjacent to the carbonyl (i.e., at the α carbon) or through electrophilic attack by HOCl at the carbon-carbon double bond.[11,21,24] In reactions with chloramine species, both carbonyl groups and carbon-carbon double bonds react slowly.[13] Under the conditions encountered in drinking water treatment systems, neither free nor combined chlorine reacts quickly enough with saturated carbonyls or olefins to cause substantial transformation of these compounds. However, the conjugated double-bond system of the α,β-unsaturated carbonyls compounds may react with free chlorine, free bromine, and combined chlorine through mechanisms that are not relevant for saturated carbonyl compounds or olefins.

To determine the potential for α,β-unsaturated carbonyls to undergo transformation reactions in water distribution systems, the reactions between these compounds and free chlorine, free bromine, and combined chlorine were studied for a range of conditions. To gain insight into the reaction mechanisms, we measured second-order rate constants for these reactions and attempted to identify products by gas chromatography-high resolution time-of-flight mass spectrometry (GC-HRT-MS) and nuclear magnetic resonance (NMR) spectroscopy. Results from this study can be used to predict the fate of these compounds in conditions encountered during chlorination in water treatment plants and in drinking water distribution systems.

Materials and Methods

Materials

Solutions were prepared with reagent grade chemicals using 18.2 MΩ Milli-Q ultra-purified water from a Millipore system. Chemicals and reagents were obtained at the highest available purity (see SI Text S1).

The dialdehydes, 2-butene-1,4-dial and 4-oxo-2-pentenal, were synthesized by hydrolysis of 2,5-dimethoxyl-2,5-dihydrofuran and 2,5-dihydro-2,5-dimethoxyl-2-methylfuran, respectively using previously described methods.[15,25] Briefly, 1 mM of the precursor compound was added to ultra-purified water that had been equilibrated with the atmosphere. After addition, the mixture was allowed to hydrolyze for at least 24 hours at room temperature to ensure complete conversion to the dialdehyde products (assumed yield > 95%).

Sodium hypochlorite (NaOCl) stock solutions (0.70 and 1.4 M) were standardized monthly by iodometric titration.[26] NaOCl working solutions (1.75 mM) were diluted from the stock and standardized at pH 10 (50 mM borate) using a Shimadzu UV-2600 spectrophotometer ($\varepsilon_{\mathrm{BrO\text{-},295\ nm}}$ = 366 M^{-1} cm^{-1}). Free bromine was produced immediately prior to use by dissolving sodium bromide (NaBr) into a standardized NaOCl solution in slight excess (1.05:1 NaBr:HOCl molar ratio). The concentration of free bromine (0.70 M) was standardized spectrophotometrically ($\varepsilon_{\mathrm{BrO\text{-},329\ nm}}$ = 332 M^{-1} cm^{-1}) after adjusting the pH of the solution to 11.[27]

Combined chlorine (i.e., chloramine) was produced immediately prior to use by adding ammonium chloride (48 mM) from a 1 M stock solution dropwise to NaOCl (40 mM). The speciation of chloramine (i.e., mono-, di-, and tri-chloramine; NH_2Cl, $NHCl_2$, NCl_3) was determined spectrophotometrically[28] after diluting the concentrated stock by a factor of 20 in buffered ultra-purified water (pH 8, 50 mM borate). The concentrations of $NHCl_2$ and NCl_3 were negligible relative to NH_2Cl (1.75 mM).

Analysis of Reaction Kinetics

Experiments to examine the reactions of nine carbonyl compounds (i.e., acrolein, methyl vinyl ketone, crotonaldehyde, trans-2-pentenal, tiglic aldehyde, 3-methyl crotonaldehyde, trans-2-hexenal, trans-2-heptenal, and 2,4-hexadienal; see Figure 4 for compound structures) with free chlorine (i.e., $HOCl/OCl^-$) were conducted under pseudo first-order conditions. Solutions containing 0.05 mM of the target compound were made by diluting stock solutions into 10 mL of 50 mM buffered solution at different pH values. To initiate an experiment, NaOCl was added to 2 mL of the buffered compound (final NaOCl concentration = 1.75 mM) in a 1-cm pathlength quartz cuvette. UV/Vis spectra of individual carbonyl compounds in excess of free chlorine were collected at equally spaced time intervals for at least two half-lives of the reaction using a Shimadzu UV-2600 spectrophotometer from 200 to 400 nm. Absorbance values at the start of the experiment were typically between 0.7 and 1.2. Wavelengths corresponding to maximum absorbance for individual compounds are listed in Table S1.

Solutions were buffered with 50 mM of either sodium acetate (pH 5.0), sodium or disodium phosphate (pHs 6.0, 7.0, 7.5, 8.0), or sodium borate (pHs 8.0, 10, 11). Sodium hydroxide and nitric acid were used to adjust the pH of the buffered solutions. The solution pH values changed by less than 0.1 units during the experiments. All experiments were conducted in triplicate unless otherwise noted. The relative standard deviation of the apparent second-order rate constants as determined from triplicate experiments was less than 10%. Second-order rate constants reported are the average of triplicates, and errors plotted in figures denote standard deviations. All experiments were conducted at temperatures ranging from 22 to 25°C.

The same approach as free chlorine was used to study the reactions of trans-2-hexenal, acrolein, and crotonaldehyde with combined chlorine (i.e., NH_2Cl), as well as the reactions of trans-2-hexenal with free bromine (i.e., $HOBr/OBr^-$). Oxidant stock solutions were added to 2 mL of buffered solutions containing the compounds in quartz cuvettes to achieve final concentrations of 1.75 mM. All reactions with NH_2Cl were conducted at pH 8.0 (buffered with 50 mM phosphate). Reactions between trans-2-hexenal and free bromine were conducted at pH values of 8.0, 8.7, 9.5, and 10.0 in 50 mM borate.

To investigate the impact of different buffers on the reaction, experiments with target compounds and free chlorine were conducted at pH 8 using both phosphate and borate buffers (50 mM). Additionally, to assess the importance of buffer catalysis, the reaction between crotonaldehyde and free chlorine was studied at varying buffer concentrations (25, 50, and 75 mM) with acetate (pH 5.0), phosphate (pH 8.0), and borate (pH 8.0) buffers.

Kinetics experiments for the reaction between crotonaldehyde and free chlorine were also analyzed using an Agilent 1260 high performance liquid chromatography (HPLC) system equipped with a UV-vis diode array detector. Experiments were conducted in a manner similar to those conducted with the UV-vis spectrophotometer by adding NaOCl (1.75 mM) to a buffered crotonaldehyde solution (0.05 mM) at pH 6 (50 mM phosphate) in a 2-mL HPLC vial. The reaction solution containing crotonaldehyde and NaOCl was injected every 6.5 minutes (50 μL injection volume, from the same vial) onto a Phenomenex Biphenyl column with an eluent mixture of pure water (90%) and 50/50 methanol/ethanol (10%) at 1.0 mL/min and 25°C (crotonaldehyde retention time = 2.6 min). Free chlorine was not quenched under these conditions because the relative decrease of crotonaldehyde over time could be determined by the known sample injection time. Crotonaldehyde peak areas were monitored over the same time scale as for the spectrophotometry experiments (i.e., > 60 minutes).

Details for additional methods are provided in the SI for: reaction kinetics (Text S2), determining rate constants for reactions between dialdehydes (2-butene-1,4-dial and 4-oxo-2-pentenal) and free chlorine (Text S3), establishing the reaction order with respect to free chlorine (Text S4), and determining activation energies for trans-2-hexenal and tiglic aldehyde (Text S5).

Analysis of Transformation Products

To prepare samples for ^{1}H NMR analysis, acrolein, crotonaldehyde, and methyl vinyl ketone were reacted with free chlorine at varying chlorine-to-organic compound ratios. The experiments employed molar concentration ratios for free chlorine to carbonyl compound of 10:1 and 1:1 (initial concentration of free chlorine = 5 mM unless otherwise stated) and reaction times (0.5 hours, 24 hours, 48 hours). Based on second-order rate constants, these conditions ensured a decrease in the concentration of each of the parent compounds by at least 90% when samples were collected at reaction times of 30 minutes or longer. Samples were prepared in D_2O with tetramethylsilane (TMS) added as an internal reference (δ 0.00) and stored at room temperature. NMR spectra were acquired on Bruker AV-700 MHz and AV-600 MHz spectrometers with 5 mm inverse probes. An AV-700 was used for ^{1}H, ^{1}H −^{1}H COSY, ^{1}H −^{13}C HSQC, and ^{1}H-^{13}C HMBC spectra. A more detailed description of the NMR analysis is included in Text S6 (SI).

To prepare samples for GC-HRT-MS analysis, crotonaldehyde and methyl vinyl ketone were chlorinated at 10:1 (initial concentration of free chlorine = 5 μM) and 1:1 chlorine-to-carbonyl-compound molar ratios. The solutions were buffered with 50 mM borate at pH 7.5 and samples were collected after 30 minutes. Samples were extracted by the addition of 1 mL methyl tert-butyl ether to 10 mL sample aliquots. Samples were shaken for 10 min and allowed to settle for 10 min. The organic layer was separated and dried of water using sodium sulfate. Controls included 5 mM and 50 mM chlorinated ultra-purified water, as well as 5 mM crotonaldehyde and methyl vinyl ketone in absence of chlorine. After extraction, samples were analyzed on a LECO GC-HRT-MS with a DB-5 column (30 m × 0.25 mm × 2.5 μm film thickness; Agilent Technologies) operated in EI high resolution (25 000; fullwidth-at-half-maximum, fwhm), with a mass range m/z 50 to 650, and ion source at 225 °C and 70 eV. Samples were injected onto the column at 35 °C using a multimode inlet. Oven temperature program details are provided in Text S7 (SI).

Results and Discussion

Reaction Kinetics

The pseudo first-order rate constants for reactions of chlorine with the aldehydes, ketone, and dialdehydes were determined in the presence of excess chlorine. The natural logarithm of the relative residual absorbance at the maximum absorption wavelength, which corresponded to the double bond adjacent to the carbonyl-carbon, was plotted against the reaction time (see Text S2 and Figure S1 in the SI). The determined pseudo first-order rate constants were converted to apparent second-order rate constants by dividing them by the total oxidant concentration. To verify the apparent second-order rate constants obtained spectrophotometrically, a rate constant was also determined by HPLC-UV for crotonaldehyde at pH 6. There was less than 2% difference between the first-order rate constants measured with the two methods (Figure S2). Pseudo first-order rate constants for the reactions of dialdehydes (i.e., 2-butene-1,4-dial and 4-oxo-2-pentenal) with free chlorine were determined under first-order conditions with excess chlorine by the same approach as above but by using the relative peak area of the adduct formed after addition of *N*-α-acetyl lysine (NAL) as determined by LC-MS/MS[29] (Figure S3).

The reaction was first order with respect to free chlorine and the carbonyl compounds for trans-2-hexenal and 3-methyl crotonaldehyde (Figure S4). Under conditions in which the carbonyl compound was present in excess of free chlorine, the species-specific rate constants for disappearance of free chlorine were within 10% of those for trans-2-hexenal and 3-methyl crotonaldehyde abatement in excess of chlorine (Figure S5).

Apparent Second-Order Rate Constants with Chlorine as a Function of pH— With the exception of 4-oxo-2-pentenal, which reacted very slowly, reactions of the carbonyl compounds with free chlorine exhibited pseudo first-order kinetics over the period of at least two half-lives, and r^2 were > 0.99 for linear regressions of the first-order plots (Table S1). For nearly all compounds, the apparent second-order rate constants increased with increasing pH, leveling out at pH values above 9 (Figure 1; Table S1). Because of the relatively low reactivity of 2-butene-1,4-dial ($k_{app} = 3.1 \times 10^{-2}$ M^{-1} s^{-1} at pH 8) and absence of reactivity of 4-oxo-2-pentenal (i.e., no change in parent compound was observed over the 10-hour duration of the experiment) with free chlorine, experiments were only conducted at pH 8 in 50 mM borate for those two compounds. No losses of target compounds or free chlorine were observed in any of the control experiments (Figure S6).

To assess the reactivities of the target compounds with bromine, experiments were conducted with trans-2-hexenal in the presence of excess of free bromine. These reactions also exhibited pseudo first-order kinetics for more than two half-lives. Apparent second-order rate constants for the reaction of the compound with free bromine were lower than those for free chlorine at pH 8 and higher than those of free chlorine at pH 10 (Figure 1c).

Due to the pH-dependent nature of the reactions between the target compounds and free chlorine, experiments were conducted to investigate potential impacts of buffer type and/or concentrations. First-order rate constants measured in solutions buffered at pH 8 in either 50 mM phosphate (pH adjusted with NaOH) or 50 mM borate exhibited relative standard deviations of less than 5% (Table S1). Rate constants were also consistent, varying by less than 4%, for experiments conducted at different buffer concentrations (e.g., 25, 50, and 75 mM) for acetate (pH 5.0), phosphate (pH 8.0), and borate (pH 8.0) (Figure S7).

α,β-Unsaturated Carbonyl Compounds and NH_2Cl—Reactions between α,β-unsaturated carbonyl compounds and combined chlorine (i.e., NH_2Cl) exhibited apparent second-order rate constants that were several orders of magnitude lower than for reactions involving free chlorine at the same total chlorine concentrations (e.g., at pH 8, $k_{app} = 8.0 \times 10^{-4}\ M^{-1}\ s^{-1}$ for the reaction of trans-2-hexenal with NH_2Cl compared to $k_{app} = 1.4\ M^{-1}\ s^{-1}$ with free chlorine; Figure S8). This agrees with previous findings in which the reactions between saturated carbonyl compounds and NH_2Cl were also too slow for transformations to be relevant over the typical residence times in drinking water distribution systems (i.e., $t_{1/2} > 100$ days for trans-2-hexenal in the presence of 2 mg L^{-1} NH_2Cl as chlorine).[30,31] Therefore, additional experiments involving NH_2Cl were only studied for the compound that exhibited the highest reactivity (i.e., acrolein) in experiments conducted at pH 8 ($k_{app,NH2Cl} = 9.9 \times 10^{-4}\ M^{-1}\ s^{-1}$).

Reactivity of Saturated Carbonyl Compounds—Reactions between saturated aldehydes and residual disinfectants were not the primary focus of this study; however, to provide a basis for comparison, experiments were conducted with representative saturated aldehydes (i.e., pentanal and hexanal) buffered at pH 8 (50 mM phosphate). These compounds reacted with free and combined chlorine with apparent second-order rate constants at pH 8 that were at least two orders of magnitude lower than for analogous α,β-unsaturated carbonyl compounds (e.g., for reactions between hexanal with free chlorine or combined chlorine at pH 8 (50 mM phosphate) $k_{app,HOCl} = 8.1 \times 10^{-3}\ M^{-1}s^{-1}$ or $k_{app,NH2Cl} = 1.3 \times 10^{-5}\ M^{-1}\ s^{-1}$ were determined, respectively).

Identification of Reactive Species

The increase in reactivity of the α,β-unsaturated carbonyl compounds with increasing pH values (Figure 1) may be related to a reaction of the deprotonated form of the hypohalous acids ($pK_a^{HOCl} = 7.58$;[32] $pK_a^{HOBr} = 8.80$[33]). At a fixed total halogen concentration, a linear correlation was observed between k_{app} and the fraction of the halogenated species that was present in the deprotonated form (i.e., α_{OCl-} and α_{OBr-}) for all compounds except 2,4-hexadienal and the two dicarbonyls (Figure 2; Figure S9).

The increase in the apparent second-order rate constant with increasing fractions of OCl^- could be attributable to a nucleophilic attack of OCl^- on the electrophilic carbonyl compounds. α,β-Unsaturated carbonyl compounds have electron-deficient β-carbon atoms, which results from the oxygen on the carbonyl-carbon withdrawing electrons from the carbon-carbon double bond. This polarization is responsible for much of the reactivity of these carbonyl compounds with nucleophilic sites on biomolecules (e.g., proteins) and explains the enhanced toxicity of this family of compounds relative to their saturated carbonyl counterparts.[14,34,35] In addition to reactions at the β-carbon, α,β-unsaturated carbonyl compounds are susceptible to nucleophilic addition at the carbonyl-carbon.[36,37] Although the exact point of OCl^- addition to α,β-unsaturated carbonyls was not determined, the trends in kinetic data suggest that OCl^- is the reactive species. The higher reactivity observed for OBr^- is consistent with the fact that OBr^- is a stronger nucleophile than OCl^- due to the lower electronegativity of bromine compared to chlorine,[38] which leads to a higher partial negative charge on the oxygen in case of OBr^-.

The only compound for which the observed second-order rate constant did not exhibit a linear increase with α_{OCl-} was 2,4-hexadienal (Figure 3a), which was the slowest reacting of the mono-carbonyl compounds. For this compound, the electron density on the carbon in the β position may have been higher compared to the other compounds due to the additional conjugated double bond. Therefore, a different reaction mechanism may have occurred for this compound with electrophilic addition involving HOCl and/or other chlorine species that are present at higher concentrations at pH values below 6 (e.g., Cl_2 or Cl_2O),[39] resulting in an observed non-linear increase in rate constants as α_{OCl-} decreased. This explanation is consistent with spectral changes observed during this reaction; as the absorbance of the conjugated bond in 2,4-hexadienal (λ_{max} = 279 nm) decreased, a new peak was observed with a maximum absorbance at 220 nM (Figure 3b). The absorbance spectrum of this new peak was similar to that of other α,β-unsaturated carbonyl compounds (e.g., trans-2-hexenal λ_{max} = 226 nm). This suggests that the double bond furthest from the carbonyl-carbon reacted with HOCl, leaving the carbon-carbon double bond in the α position relative to the carbonyl-carbon intact. Therefore, α,β-unsaturated carbonyl compounds with two conjugated double bonds (e.g, 2,4-hexadienal) likely have different reaction mechanisms and nucleophilic addition of OCl^- might not be as important as it is for compounds with a single double bond (e.g., acrolein and crotonaldehyde).

Effect of Carbonyl Compound Structure on Reactivity

Species-specific second-order rate constants for reactions of carbonyl compounds other than 2,4-hexadienal and 2-butene-1,4-dial with OCl^- (k_{OCl-}) ranged from 0.21 to 12 M^{-1} s^{-1} (Table S2). Apparent second-order rate constants for the reactions between the α,β-unsaturated carbonyl compounds and free chlorine (k_{app}) ranged from 3.1×10^{-2} to 8.6 M^{-1} s^{-1} at pH 8 (Figure 4; Table S2) and from 7.6×10^{-2} to 2.6 M^{-1} s^{-1} at pH 7 (Table S2). Acrolein, the simplest of the α,β-unsaturated carbonyl compounds, exhibited the highest reactivity. As electron-donating groups (e.g., alkyl groups) were added to either the carbonyl-carbon or the β-carbon, the apparent second-order rate constants at pH 8 decreased (Figure 4). The effect of substituents was most pronounced with the addition of a methyl group to the carbonyl-carbon (i.e., acrolein vs. methyl vinyl ketone), which lowered the apparent second-order rate constant by over an order of magnitude. This is likely due to a partial compensation of the electron withdrawing effect of the carbonyl group by the electron donating effect of the alkyl substituent. This substituent effect was also pronounced for the addition at the first methyl group to the β-carbon (i.e., a 72% decrease in k_{app} was observed between acrolein and crotonaldehyde), with smaller additional decreases from the addition of ethyl groups (i.e., a 29% decrease in k_{app} was observed between crotonaldehyde and trans-2-pentenal, 20% between trans-2-pentenal and trans-2-hexenal, and 11% between trans-2-hexenal and trans-2-heptenal).

Addition of alkyl groups to the β-carbon (e.g., 3-methyl crotonaldehyde) further lowered the apparent second-order rate constant, likely because of the greater electron donating capacity of two methyl groups at the β-carbon as opposed to a single ethyl group (i.e., trans-2-pentenal). Branching at the α-carbon (e.g., tiglic aldehyde) had a greater effect on the apparent second-order rate constant, possibly due to the lack of α-hydrogens, which appear to be important to the reaction. As discussed previously, 2,4-hexadienal exhibited much lower second-order rate constants than the α,β-unsaturated carbonyl compounds that did not contain a second carbon-carbon double bond. The dialdehyde, 2-butene-1,4-dial, exhibited a lower second-order rate constant than 2,4-hexadienal, and 4-oxo-2-pentenal did not exhibit any reactivity, possibly due to inhibition of the conjugation.

Fate of α,β-Unsaturated Carbonyls during Disinfection and Distribution

Depending on the source water quality and treatment, the applied free chlorine doses during disinfection typically range from 1 to 4 mg L^{-1}.[40] During disinfection of the distribution system, water utilities typically try to achieve a residual of approximately 1 mg L^{-1} Cl_2.[41] If α,β-unsaturated carbonyl compounds persist after the initial disinfection step, their transformations in a distribution system with a residual of 1 mg L^{-1} Cl_2 and a pH of 8 can be assessed by considering the predicted half-lives, which range from 1.6 to 440 h (Figure 4; Table S2). Except for tiglic aldehyde, 2,4-hexadienal, and the dialdehydes, a substantial fraction of the unsaturated carbonyl compounds should react with free chlorine prior to reaching a consumer’s tap (i.e., half-lives range from 1.6 to 91 h and average hydraulic residence times in a distribution system typically range from 24–96 h).[42] Lower operational pH values, which lead to better disinfection efficiency, will result in longer half-lives for slower-reacting compounds (e.g., at pH 7, the half-life of tiglic aldehyde is 180 h compared to 77 h at pH 8; Table S2). Based on the activation energy of the reaction of selected α,β-unsaturated carbonyls with free chlorine (i.e., 60–70 kJ mol^{-1}; Figure S10), lower water temperatures also will increase the half-lives. For example, the half-life of tiglic aldehyde increases from 91 hours at 25°C to 213 hours at 15°C. If monochloramine is used as a disinfectant residual, little, if any, reaction would be expected.

Tentative Identification of Transformation Products

Products from the reaction of free chlorine with acrolein, crotonaldehyde, and methyl vinyl ketone were analyzed by ^{1}H NMR (Text S9). In the NMR spectra from experiments with equimolar chlorine and carbonyl concentrations, the absence of any signal from the carbon-carbon double bond for acrolein or crotonaldehyde suggests that the α and/or β carbon of the product were fully saturated, providing evidence for loss of the olefinic bond (Figures S11 and S14). This supports the observations of a decrease in absorbance corresponding to loss of the carbon-carbon double bond during UV/Vis kinetics experiments. The equimolar reaction conditions also resulted in the apparent loss of the aldehyde group, which is likely a result of rearrangement involving the aldehyde to form a stable gemdiol species (Product A in Scheme 1 and Figure S20; Figures S11, S14 and S17).

Experiments using a 10:1 molar excess of chlorine produced multiple products which changed with time (Figures S12, S15, and S18). Product A, the substituted gemdiol-like species, which was the major product at the equimolar chlorine to carbonyl condition, was also the main product observed after 30 minutes. However, it was not observed in the spectra measured after 1 or 2 days. In the presence of excess chlorine, further reaction of this product and/or rearrangement resulted in a product with a carbonyl group and additional chlorine atoms or hydroxyl groups (Product B) after 1 or 2 days (Scheme 1, Figures S13, S16, S19, and S20). In the case of acrolein, two additional substituted products with only one active NMR signal each, a probable gemdiol (Product C) and a diketone (Product D), were also observed (Scheme 1, Figures S12 and S20). Crotonaldehyde and methyl vinyl ketone also yielded similar final products (Figure S20).

Although the NMR data are insightful, there is not enough information to unambiguously identify the products of these reactions without reference spectra from analytical standards. For example, in Products B and C, the “Z” symbol could be attributable to either -OH or -Cl (Scheme 1; Figure S20). While the -Cl substituted products might be unstable in water and readily hydrolyze, there is no strong evidence of a carboxylic acid group (i.e., -OH) in the ^{1}H NMR spectra. Additional research is needed to confirm these substituents using reference compounds.

The formation of multiple halogenated transformation products was supported by analysis of spectra from peaks observed in the GC-HRT-MS analysis of chlorinated crotonaldehyde and methyl vinyl ketone. Although the GC-HRT-MS data did not contain masses corresponding to the structures depicted in Scheme 1, polyhalogenated compounds including chloroform and trichloroacetaldehyde were detected. These compounds accounted for about 3% of the carbonyl compound loss at a 10:1 ratio of chlorine-to-carbonyl compound (Figures S21 and S22). The identification of these polyhalogenated minor products supports the notion of multiple reaction pathways and, most likely, multiple chlorine substitutions. Other oxygenated compounds (e.g., 2,3-butanedione and/or 3-oxobutanal, and 2-oxobutanal) were also tentatively identified by accurate mass (Figures S23 and S24) from the chlorination of crotonaldehyde and methyl vinyl ketone. It is likely that multiple reactions with chlorine led to an array of chlorine- and oxygen-substituted products formed in low yields by different and competing pathways.

Practical Implications

α,β-Unsaturated carbonyl compounds are electrophilic compounds that have the potential to damage cells by forming covalent bonds with nucleophilic biological targets (e.g., proteins, DNA). In water treatment systems, the concentration of α,β-unsaturated carbonyl compounds will likely decrease when chlorine is used during drinking water disinfection or as a residual disinfectant in distribution systems. The most reactive α,β-unsaturated carbonyl compounds (e.g., acrolein, crotonaldehyde) will be transformed prior to reaching the consumer’s tap if free chlorine is used. The main products of this reaction, which lack the unsaturated carbon bond, appear to be stable for up to 48 hours, suggesting some potential for human exposure through drinking water. The least reactive carbonyl compounds, including tiglic aldehyde, and the dicarbonyls 2,4-butenedial and 4-oxo-2-pentenal, will not be transformed to an appreciable degree during disinfection or in a distribution system. Furthermore, little, if any, change in concentrations of any of the compounds will occur when chloramine is used for disinfection or as a residual disinfectant. Although nucleophilic addition can also occur with OBr^-, these reactions will not be as much of a concern due to the higher pK_a of $HOBr/OBr^-$ and low bromide concentrations typically found in drinking water (Text S6, Figure S25).

It is difficult to assess the health implications of this reaction because the toxicities of the putative products of the reactions of α,β-unsaturated carbonyl compounds with OCl^- are mostly unknown. The reaction almost certainly results in the loss of electrophilic character (i.e., disappearance of the carbon-carbon double bond in α position to the carbonyl), which is responsible for the enhanced toxicity of the α,β-unsaturated compounds. As a result, the products of the reaction might have a lower affinity for proteins and DNA, rendering them less toxic than the parent compounds. The chlorinated products identified during GC-HRT-MS analysis likely exhibit different modes of toxicity compared to the parent carbonyls, and many compounds with these structures are known or suspected carcinogens.[43,44] However, the yields of these products were low. Additional research is needed to further elucidate the structures of the major transformation products formed in the presence of chlorine, and to initiate efforts to assess the risks associated with their presence in drinking water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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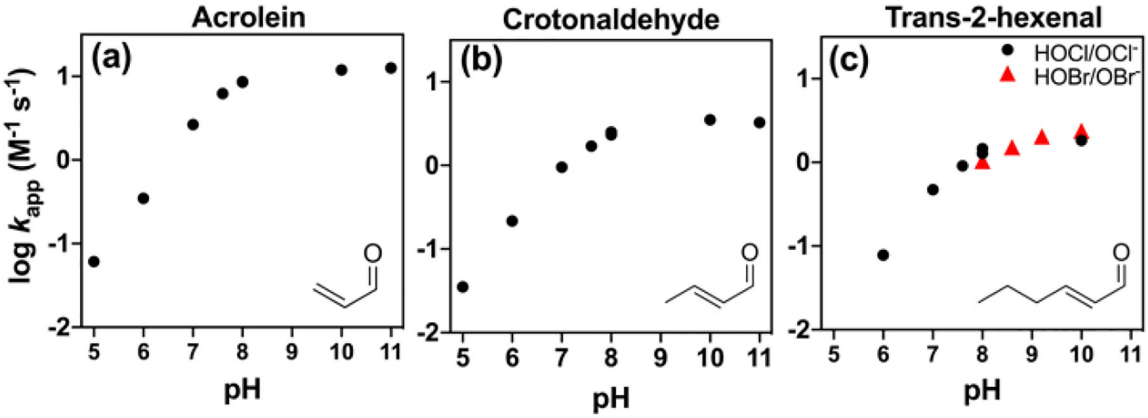


Figure 1.

Apparent second-order rate constants (k_{app}) as a function of pH for the reactions of (a) acrolein; (b) crotonaldehyde; and, (c) trans-2-hexenal with free chlorine (black circles). (c) Apparent second-order rate constants for the reaction of trans-2-hexenal with free bromine (red triangles) are also shown. Experimental conditions: initial aldehyde concentrations were 0.05 mM and oxidant doses were 1.75 mM to establish first order conditions. Symbols represent the average and error bars represent the standard deviation (n=3); error bars not shown are smaller than the size of the markers.

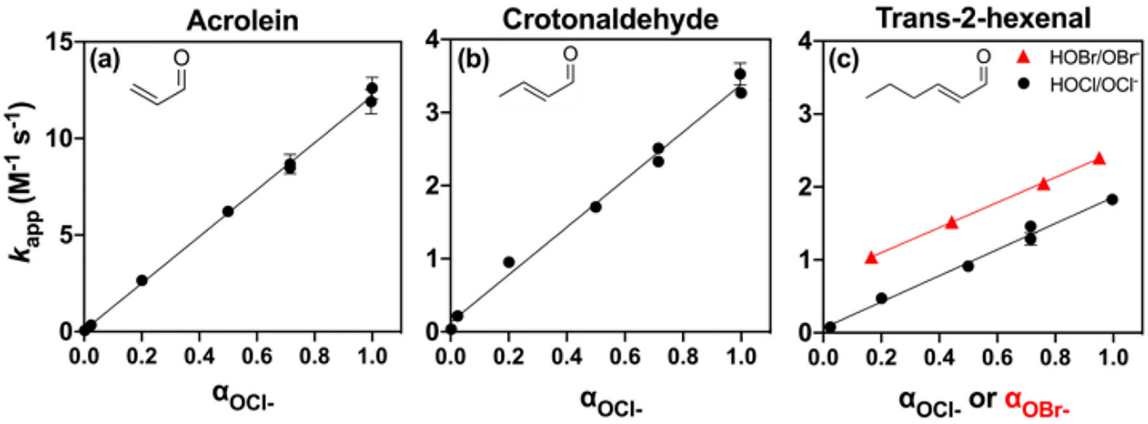


Figure 2.

Apparent second-order rate constants (k_{app}) for reactions of target compounds with free chlorine (black circles) as a function of α_{OCl-} for (a) acrolein; (b) crotonaldehyde; and, (c) trans-2-hexenal. (c) Experiments were also conducted with trans-2-hexenal in the presence of free bromine (red triangles), and the respective apparent second-order rate constants are plotted against α_{OBr-}. Experimental conditions: initial aldehyde concentrations were 0.05 mM and total oxidant concentrations were 1.75 mM. Symbols represent the average and error bars represent the standard deviation (n=3); error bars not shown are smaller than the size of the markers.

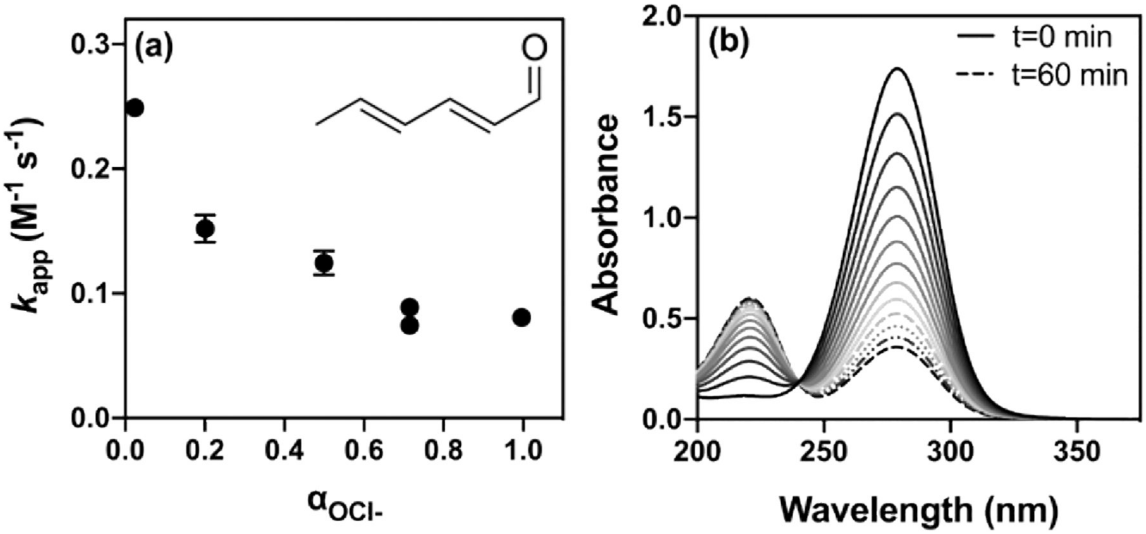


Figure 3.

(a) Apparent second-order rate constants (k_{app}) for reactions between 2,4-hexadienal and free chlorine as a function of α_{OCl-}. (b) Evolution in absorbance spectra of 2,4-hexadienal in the presence of 1.75 mM free chlorine at pH 6 (50 mM phosphate) with the peak at 279 nm disappearing and a new peak growing at 220 nm. Spectra were measured every 5 min up to 60 min. Initial 2,4-hexdienal concentration was 0.05 mM.

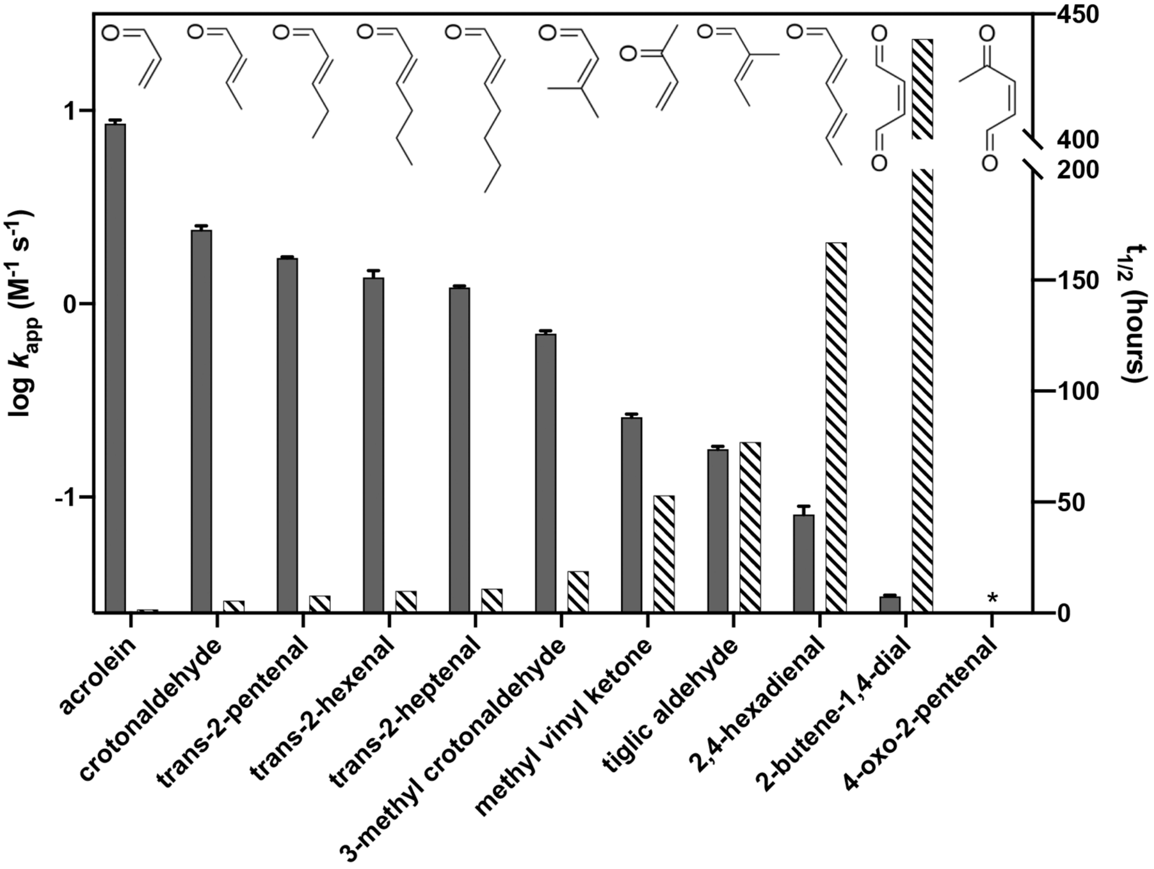
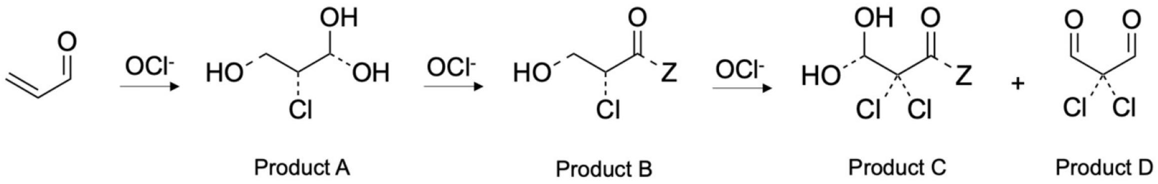


Figure 4.

Apparent second-order rate constants (k_{app}, solid bars) and corresponding half-lives ($t_{1/2}$, hatched bars) at pH 8 for reactions between α,β-unsaturated carbonyl compounds and free chlorine. Half-lives were calculated assuming a free chlorine concentration of 1 mg L^{-1} as Cl_2. Average and standard deviations are shown for experiments conducted in 50 mM borate and phosphate buffers; n=6 for all compounds except for 2-butene-1,4-dial (n=3). *The rate constant for 4-oxo-2-pentenal was not measurable due to the slow rate of the reaction.



Scheme 1.

Suggested structures for the major NMR active products of acrolein in the presence of excess chlorine. Structures indicate an initial loss of the carbon-carbon double bond (Product A), and a mixture of probable final product (Products B, C, and D). Dashed lines show the most probable substituents and -Z corresponds to -OH or -Cl.