

Chlorpyrifos Transformation by Aqueous Chlorine in the Presence of Bromide and Natural Organic Matter

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The aqueous chlorination of chlorpyrifos (CP) was investigated in the presence of bromide and natural organic matter (NOM), which were identified as naturally occurring aqueous constituents that could affect CP transformation rates to the toxic product chlorpyrifos oxon (CPO). Bromide can be oxidized by chlorine to form hypobromous acid (HOBr), which was found to oxidize CP at a rate that was 3 orders of magnitude faster than was the case with chlorine: $k_{\text{HOBr,CP}} = 1.14 (\pm 0.21) \times 10^9 \text{ M}^{-1} \text{ h}^{-1}$ and $k_{\text{HOCl,CP}} = 1.72 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$, respectively. Similar to previous findings with the hypochlorite ion, hypobromite (OBr^-) was found to accelerate the hydrolysis of CP and CPO: $k_{\text{OBr,CP}} = 965 (\pm 110) \text{ M}^{-1} \text{ h}^{-1}$ and $k_{\text{OBr,CPO}} = 1390 (\pm 160) \text{ M}^{-1} \text{ h}^{-1}$, respectively. Treated water from the Athens-Clarke County (ACC) water treatment plant in Athens, GA, was used in some of the experiments as a NOM source. A mechanistic model was used to adequately predict the loss of CP as well as the formation of CPO and the hydrolysis product 3,5,6-trichloro-2-pyridinol (TCP) in the presence of the ACC water.

KEYWORDS: Chlorpyrifos; organophosphorus (OP) pesticides; chlorination; drinking water treatment; modeling; reaction pathways

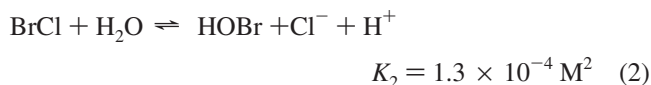
INTRODUCTION

The Food Quality Protection Act (FQPA) of 1996 requires that all potential exposure routes be assessed to determine whether pesticide tolerances will be exceeded. Drinking water is considered to be a dietary exposure pathway; however, few studies have examined the fate of pesticides in the presence of free chlorine under conditions similar to drinking water treatment. Chlorination is the most commonly used chemical disinfection process for community water systems (1), and chlorine is known to react with some pesticides such as *s*-triazines, carbamates (2–6), and organophosphorus (OP) pesticides (7–9).

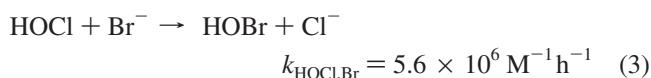
When chlorine reacts with the phosphorothioate subgroup of OP pesticides, the thiophosphate functionality (P=S) can be oxidized to its corresponding oxon (P=O) (7–9). The resulting oxons are typically more potent than the parent as an inhibitor of acetylcholinesterase, an enzyme necessary for regulating nerve impulse transmission between nerve fibers (9). Duirk and Collette (10) elucidated the fate of chlorpyrifos (CP) and its transformation products over the pH range of 6.3–11 in the presence of aqueous chlorine. They were able to model the rapid oxidation of CP by HOCl, resulting in the more toxic chlorpyrifos oxon (CPO) and hydrolysis of CP and CPO to 3,5,6-trichloro-2-pyridinol (TCP), as well as hypochlorite-assisted hydrolysis of CP and CPO to TCP over this pH range in buffered deionized water systems. However, naturally oc-

curing aqueous constituents such as bromide ion and natural organic matter (NOM) may affect the transformation rates for OP pesticides during drinking water treatment.

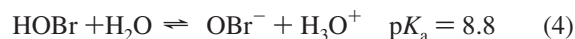
Bromide can be easily oxidized to hypobromous acid (HOBr), which is a stronger oxidant than HOCl, in the presence of aqueous chlorine (11). Upon initial reaction, Cl^+ is transferred to Br^- , resulting in the formation of bromine chloride (BrCl), which rapidly hydrolyzes to HOBr (12).



Under drinking water treatment conditions, the equilibria in eqs 1 and 2 favors the forward reactions resulting in the overall stoichiometry and second-order rate coefficient (11).



In the presence of excess chlorine, all bromide present will be oxidized to hypobromous acid (13). Because the $\text{p}K_a$ of hypobromous acid is 8.8 (11), HOBr will be the dominant brominated oxidant over the drinking water pH range of 6.5–9.



Therefore, it is believed that the presence of bromide under drinking water treatment conditions could accelerate the trans-

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formation rate of anthropogenic chemicals. For example, the rate coefficient for HOBr reacting with pyrene was found to be 2 orders of magnitude faster than that for HOCl in aqueous solutions (14). Westerhoff et al. (15) conducted a nationwide survey of 101 drinking water sources in the United States and found an average bromide concentration of $\approx 1.25 \mu\text{M}$. Because bromide is relatively ubiquitous and 90% of community drinking water systems use chlorine for both primary and secondary disinfection, the presence of bromide in drinking water sources could affect the rate of organophosphorus (OP) pesticide transformation in chlorinated potable water.

The presence of NOM in drinking water sources has also been a primary concern for the drinking water industry. The physical–chemical characteristics of NOM are a function of decaying organic matter from both terrestrial and aquatic sources, environmental conditions, and microorganisms present in the watershed (16). Hence, the composition and concentration of NOM in source waters fluctuates from source to source and often varies within each source depending on conditions such as rainfall, change in seasons, and temperature. When chlorine is added to treated water containing bromide and NOM, both brominated and chlorinated oxidants react with NOM, resulting in the formation of disinfection byproducts (DBPs) (17, 18). Also, the brominated DBPs are believed to be more carcinogenic than their chlorinated analogues (19). The electron density (i.e., aromaticity) of NOM is often expressed as specific ultraviolet absorbance (SUVA), which is the ratio of ultraviolet absorbance of the NOM at a specific wavelength divided by the total organic carbon concentration (TOC) in milligrams of C per liter. This specific physical–chemical property has been found to correlate to reactivity of NOM with free chlorine and serve as a reliable surrogate for DBP formation (20, 21). Because both chlorinated and brominated oxidants react with NOM (22), the presence of NOM can potentially act as a sink for active oxidants in finished drinking water. Thus, its presence can impact the rate of OP pesticide transformation under drinking water treatment conditions.

The influence of bromide and NOM was investigated to determine their effect on the transformation of CP by aqueous chlorine. The influence of bromide was investigated as a function of concentration and pH of the aqueous system at chlorine concentrations representative of drinking water treatment. To further elucidate transformation pathways, native hypobromous acid was used to determine intrinsic rate coefficients for the oxidation of CP to CPO as well as hypobromite-assisted hydrolysis of CP and CPO to TCP. Treated effluent from the Athens-Clarke County (ACC) water treatment plant in Athens, GA, was collected prior to chlorination and used in kinetic experiments. Experimental results were then compared to predictions from an existing numerical model that did not account for the influence of either NOM or bromide (10). The work reported here serves to further elucidate the OP transformation pathways under drinking water treatment conditions.

MATERIALS AND METHODS

Chlorpyrifos (99.5%), chlorpyrifos oxon (98.7%), and 3,5,6-trichloro-2-pyridinol (99%) were purchased from ChemService (West Chester, PA). Commercial 10–13% sodium hypochlorite (NaOCl) was purchased from Aldrich (Milwaukee, WI). Saturated bromine water, which was approximately 1.3% active bromine, was purchased from Fisher Scientific (Pittsburgh, PA). Aqueous stock solutions and experiments utilized laboratory-prepared deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$) from a Barnstead ROPure Infinity/NANOPure system (Barnstead-ThermoLyne Corp., Dubuque, IA). Phosphate and carbonate salts used for buffer solutions were dissolved in deionized water and filtered through a $0.45 \mu\text{M}$ filter purchased from Millipore (Billerica, MA), which was

Table 1. NOM and Source Water Characteristics for the ACC Water Collected prior to Chlorination

source	SUVA ₂₅₄ [L/(m mg)]	SUVA ₂₈₀ [L/(m mg)]	[NH ₃] _T ^a (μM)	[Cl ⁻] (μM)	[NO ₂ ⁻] (μM)	[Br ⁻] (μM)	[PO ₄] _T ^b (μM)	[SO ₄ ²⁻] (μM)
ACC	1.61	1.07	2.06	93.46	0.04	0.15	ND ^c	8.30

^a [NH₃]_T = [NH₄⁺] + [NH₃]. ^b [PO₄]_T = [H₃PO₄] + [H₂PO₄⁻] + [HPO₄²⁻] + [PO₄³⁻]. ^c Not detected.

prerinsed with deionized water. The pH for the experiments was adjusted with either 1 N H₂SO₄ or NaOH. All other organic and inorganic chemicals were certified ACS reagent grade and used without further purification. The glassware and polytetrafluoroethylene (PTFE) septa used in this study were soaked in a concentrated free chlorine solution for 24 h, rinsed with copious amounts of deionized water, and dried at 105 °C prior to use. All chlorination experiments were conducted at constant temperature (25 ± 1 °C).

Water was collected from the Athens-Clarke County (ACC) water treatment plant in Athens, GA, and used in the experiments investigating the effect of NOM on CP degradation kinetics. The ACC water treatment facility uses conventional physical–chemical surface water treatment (i.e., coagulation, flocculation, sedimentation, and dual media filtration). Water was collected prior to chlorination and was filtered through a $0.45 \mu\text{M}$ filter. The ACC water and NOM characteristics are shown in Table 1. The SUVA₂₅₄ of the ACC effluent was 1.61 L/(mg m), which indicates a low aquatic humic substance concentration (20).

For all oxidation experiments, CP was spiked by adding 0.5 mL of a 4 mM stock solution in ethyl acetate into an empty 4 L borosilicate glass Erlenmeyer flask. A gentle flow of nitrogen gas was used to evaporate the ethyl acetate, and then 4 L of deionized or ACC water was added to the flask. The solution was slowly stirred at a pH of 6.5–7 and allowed to dissolve for 12 h resulting in an aqueous CP concentration of $0.5 \mu\text{M}$, and hydrolysis of CP over this pH range was negligible (23). When called for, bromide was added to the aqueous system prior to chlorination. CP oxidation kinetic experiments were conducted under pseudo-first-order conditions: total chlorine to chlorpyrifos molar ratios of 20:1, 50:1, 100:1, and 200:1. Chlorine or bromine was added to solutions under rapid mix conditions achieved with a magnetic stir plate and a PTFE-coated stir bar. All kinetic experiments used to determine rate coefficients were conducted until 87% loss of parent compound was observed.

Above pH 8, 10 mM carbonate [CO₃]_T buffer was used to maintain pH. The commercial free chlorine solution was first diluted to 14 mM and then added to the aqueous system containing $0.5 \mu\text{M}$ chlorpyrifos and carbonate buffer in a 2 L Erlenmeyer flask. Fourteen aliquots from the large 2 L reactor were then placed into 128 mL amber reaction vessels with PTFE septa and stored in the dark. In the pH range of 6.5–7.5, the rate of CP loss in the presence of free chlorine was very rapid. Therefore, 14 100-mL aliquots of the 2 L aqueous system containing 10 mM phosphate buffer, [PO₄]_T, and $0.5 \mu\text{M}$ CP were placed in 250 mL amber Erlenmeyer flasks. Then each flask was individually dosed with the appropriate amount of chlorine under rapid mix conditions. This type of reactor has been successfully shown to work for investigating halogenated oxidants reacting with aqueous constituents when the reaction is not diffusion-controlled (24).

At each discrete sampling interval, two reaction vessels were sacrificed in their entirety. One vessel was used to determine total free chlorine concentration ([HOCl]_T = [HOCl] + [OCl⁻]) via Standard Method 4500-Cl F DPD-FAS titrimetric method (25). In the other vessel, free chlorine residuals were quenched with sodium sulfite in 20% excess of the initial free chlorine concentration and the pH of a 100 mL sample was then adjusted to 2 for analysis of CP and its degradation products. Holding studies have been performed previously, and sulfite was found not to interact with CP or its transformation products (10).

CP and its degradation products were extracted from water using C-18 solid phase extraction cartridges purchased from Supleco (Bellefonte, PA). The 100 mL sample was adjusted to pH ≤ 2 to increase the recovery of TCP ($\text{p}K_a = 4.55$) on the solid phase adsorbent (26). Then, the sample was spiked with $1 \mu\text{M}$ phenthorate (internal standard), mixed

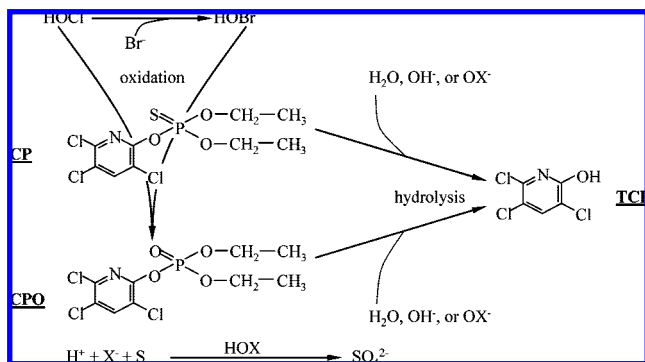


Figure 1. Schematic of CP transformation pathways in the presence of aqueous chlorine and bromide. HOX represents either HOCl or HOBr, and X⁻ can represent either Cl⁻ or Br⁻.

thoroughly by hand for 2 min, passed through the SPE cartridge at an approximate flow rate of 7 mL/min, and eluted with 3 mL of ethyl acetate. Quantification for each analyte was compared to eight extracted standards over the concentration range of 0.01–1 μ M. A Hewlett-Packard 6890 GC equipped with a 5973 MSD was used to analyze CP, CPO, and TCP. GC conditions were as follows: 30 m Restek Rtx-200 column with a 0.25 mm i.d. and 0.5 μ m film thickness. The temperature profile was as follows: 100 °C for 5 min, raised from 100 to 250 at 10 °C/min, and then held at 250 °C for 25 min. Mass balances of 80% or greater were obtained for each experiment.

UV-vis spectra were acquired with a Shimadzu 1700 UV-vis spectrometer (Shimadzu Scientific, Columbia, MD). Total organic carbon (TOC) was measured using a Shimadzu TOC 5000 (Shimadzu Scientific) and calibrated according to Standard Method 505A (25). Ion chromatography was performed on a Metrohm (Houston, TX) MIC-2 ion chromatograph with chemical suppression. Total ammonia ($[\text{NH}_3]_{\text{T}} = [\text{NH}_4^+] + [\text{NH}_3]$), chloride, nitrite, bromide, phosphate, and sulfate were all calibrated over the concentration range from 0 to 100 μ M. All pH measurements were obtained with an Orion 940 pH-meter using a Ross combination electrode from Fisher Scientific (Pittsburgh, PA).

RESULTS AND DISCUSSION

Loss of CP in the Presence of Bromide and Aqueous Chlorine. The transformation pathways of CP in the presence of aqueous chlorine and bromide are relatively complicated (Figure 1). The known transformation pathways are (1) HOCl oxidation of CP resulting in CPO formation, (2) OCl⁻-assisted hydrolysis of CP and CPO, and (3) hydrolysis of CP and CPO. Figure 1 also shows the formation of HOBr and the proposed pathways of brominated oxidants reacting with CP and CPO, which are HOBr oxidation of CP and OBr⁻-assisted hydrolysis of CP and CPO. Prior to the determination of the intrinsic rate coefficients for these pathways, the influence of bromide on the overall observed rate of CP loss was determined at bromide concentrations relevant to drinking water treatment conditions.

Experiments to determine if bromide does accelerate the rate of CP loss were conducted over the pH range of 7–9, $[\text{CP}] = 0.5 \mu\text{M}$, $[\text{HOCl}]_{\text{T}} = 10$ and 50 μM , with increasing bromide concentrations from 0 to 10 μM . At $[\text{HOCl}]_{\text{T}} = 10 \mu\text{M}$ (Figure 2), k_{obs} was found to increase linearly as bromide concentrations were increased over the pH range investigated. This was also observed at the higher chlorine concentration of 50 μM (Figure 3). Furthermore, at a given chlorine dose, the slopes of the regression lines in Figures 2 and 3 vary in a systematic way as a function of pH and bromide concentration. The rate of CP loss appears to be dependent on the concentration of bromide, chlorine, and pH. This indicates that bromide could be acting as a catalyst via HOBr formation.

At lower bromide concentrations (0.1 and 1.0 μM) and chlorine concentration of 10 μM , CP is competitive with

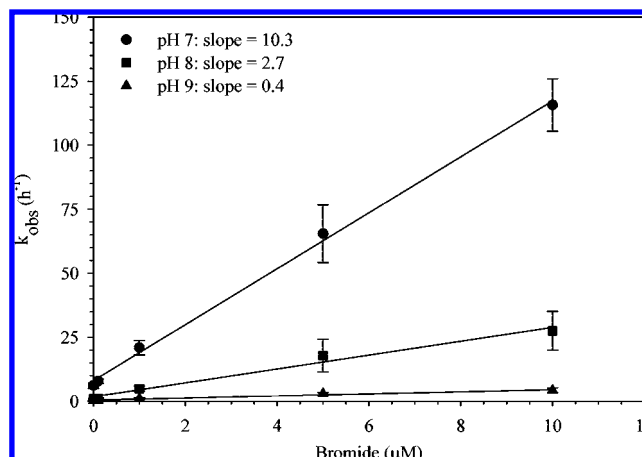


Figure 2. Observed first-order rate coefficients for CP loss in the presence of increasing bromide and $[\text{HOCl}]_{\text{T}} = 10 \mu\text{M}$ over the pH range of 7–9. $[\text{CP}]_0 = 0.5 \mu\text{M}$, $[\text{buffer}]_{\text{T}} = 10 \text{mM}$, and temperature = 25 °C.

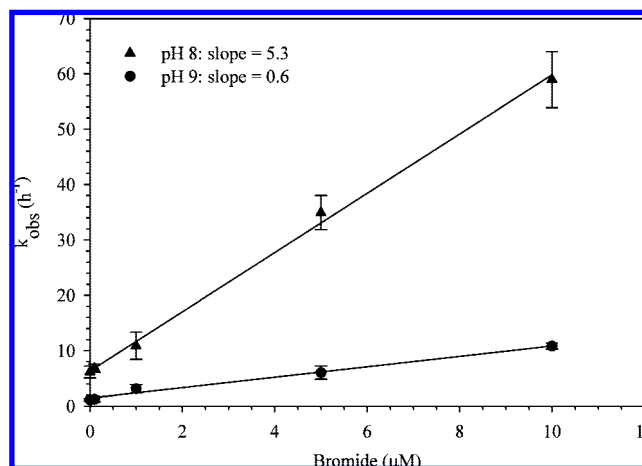


Figure 3. Observed first-order rate coefficients for CP loss in the presence of increasing bromide and $[\text{HOCl}]_{\text{T}} = 50 \mu\text{M}$ at pH 8 and 9. $[\text{CP}]_0 = 0.5 \mu\text{M}$, $[\text{CO}_3]_{\text{T}} = 10 \text{mM}$, and temperature = 25 °C.

bromide for oxidation by HOCl. In the presence of excess chlorine, all bromide present would be oxidized to its active form (HOBr) (13). Therefore, the oxidation of CP is most likely carried out by both HOCl and HOBr at low bromide concentrations. As bromide concentrations increased to 5.0 and 10.0 μM , HOCl is more likely to oxidize bromide than CP as chlorine to bromide molar ratios approach 1. For example, at the 10 μM chlorine concentration, addition of 10 μM of bromide induced ~20- and ~30-fold increases in k_{obs} at pH 9 and 8, respectively, compared to the absence of bromide. However, the addition of 10 μM bromide at the 50 μM chlorine increased the k_{obs} only ~4- and ~10-fold at pH 9 and 8, respectively, when compared to the CP loss rates in the absence of bromide. The reaction rate coefficient for HOCl with bromide ($k_{\text{HOCl,Br}} = 5.6 \times 10^6 \text{M}^{-1} \text{h}^{-1}$) is approximately 3 times faster than HOCl with CP ($k_{\text{HOCl,CP}} = 1.7 \times 10^6 \text{M}^{-1} \text{h}^{-1}$) (10, 11). When bromide concentrations are 0.1–1.0 μM , HOCl is the primary oxidant responsible for the loss of CP. However, when $[\text{HOCl}]_{\text{T}}/[\text{bromide}]$ molar ratios approach unity, HOBr appears to become the primary oxidant. Therefore, the magnitude of bromide-catalyzed oxidation of CP is controlled by the ratio of HOCl to bromide as well as pH.

HOBr formation is ultimately controlled by the pH of the aqueous system. Because the $\text{p}K_{\text{a}}$ of HOCl is 7.5, the percentages of free chlorine present as HOCl were approximately 75,

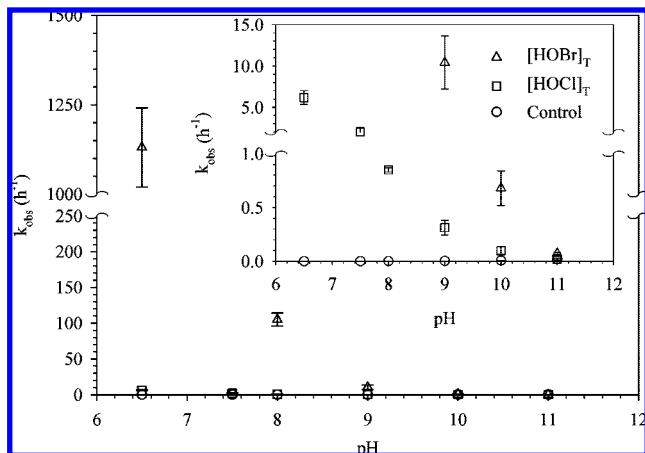


Figure 4. Observed first-order loss rates of CP over the pH range of 6.5–11 with either aqueous bromine or chlorine. $[CP]_0 = 0.5 \mu\text{M}$, $[\text{oxidant}]_T = 10 \mu\text{M}$, $[\text{buffer}]_T = 10 \text{mM}$, and temperature = $25 \pm 1 \text{ }^\circ\text{C}$. The inset shows the first-order observed rate coefficients for the controls and in the presence of chlorine more clearly. Error bars represent 95% confidence intervals.

23, and 3% at pH 7, 8, and 9, respectively. HOCl is the only chlorine species under these experimental conditions capable of oxidizing bromide to HOBr (eqs 1–3) (11, 12). The magnitude of bromide-catalyzed oxidation of CP as a function of pH is clearly demonstrated by examining the slopes of the regression lines (Figures 2 and 3). At pH 7, HOCl is the dominant chlorine species available to react with bromide. In the presence of increasing bromide concentration, the increased HOBr formation rate increases the observed rate of CP loss at pH 7. At pH 8 and 9, the slopes of the regression lines are significantly less than at pH 7. This demonstrates that bromide-catalyzed CP oxidation is dependent on the concentrations of bromide and chlorine as well as the pH, which determines chlorine speciation. Therefore, bromide is a catalyst in the oxidation of CP because it increased the observed rate of CP loss and does not appear in the overall stoichiometry of the reaction mechanism. Bromide is first oxidized by HOCl, resulting in HOBr, which oxidizes CP, yielding H^+ and Br^- . The regenerated bromide ion can be reoxidized by HOCl and participate in additional reactions with CP (Figure 1).

Bromine Reactions with CP. In the presence of chlorine, bromide was found to catalyze the loss of CP via the formation of HOBr. To further investigate this phenomenon, the reaction of native bromine with CP was investigated over the pH range of 6.5–11 in the presence of excess bromine (Figure 4). At pH 6.5, the first-order observed loss of CP was 3 orders of magnitude greater in the presence of HOBr than for HOCl under similar experimental conditions. Even at pH 8 and 9, the observed rate of CP loss in the presence of bromine was still significantly greater than with chlorine. Because the $\text{p}K_a$ of HOBr is 8.8, approximately 86.3 and 38.7% of bromine would be in the HOBr form at pH 8 and 9, respectively. At pH 10 and 11, bromine does not have as significant an effect on the k_{obs} because $<0.06\%$ of bromine is in the HOBr form. However, as shown in Figure 4 HOBr reacts significantly more rapidly than HOCl over the entire drinking water pH range of 6.5–9. Similarly with chlorine, bromine was added at increasing concentrations to determine the stoichiometry for both HOBr and CP. HOBr was found to be first-order with respect to bromine under pseudo-first-order conditions. When $\log(k_{obs})$ was plotted versus $\log[\text{HOBr}]_T$ at pH 11 and $[\text{HOBr}]_T = 10, 25, 50,$ and $100 \mu\text{M}$, the slope of the line was approximately 1,

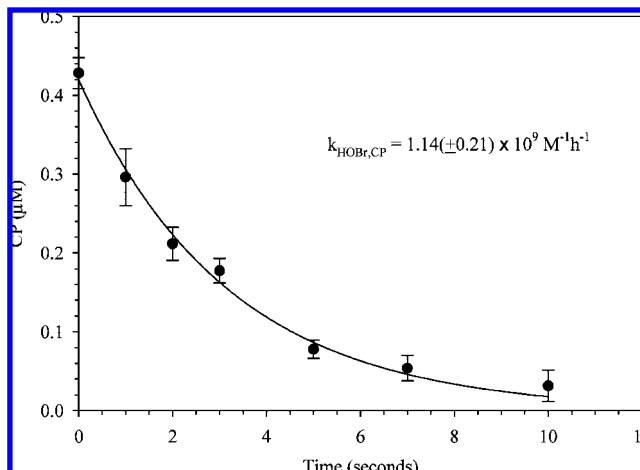


Figure 5. Second-order rate coefficient for the reaction between hypobromous acid and CP at pH 6.5. $[CP]_0 = 0.43 \mu\text{M}$, $[\text{HOBr}]_T = 10 \mu\text{M}$, $[\text{PO}_4]_T = 10 \text{mM}$, and temperature = $25 \pm 1 \text{ }^\circ\text{C}$. Error bars represent 95% confidence intervals.

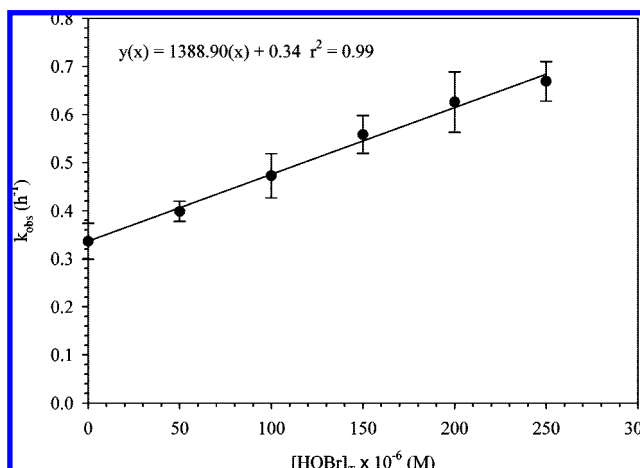


Figure 6. Second-order rate coefficient for bromine-assisted hydrolysis of CPO at pH 11. $[\text{CPO}]_0 = 0.5 \mu\text{M}$, $[\text{HOBr}]_T = 0\text{--}250 \mu\text{M}$, $[\text{buffer}]_T = 10 \text{mM}$, and temperature = $25 \pm 1 \text{ }^\circ\text{C}$. Error bars represent 95% confidence intervals.

indicating that CP was also first-order, yielding an overall second-order reaction for the loss of CP in the presence of bromine, which was similar to the results for CP loss in the presence of aqueous chlorine (10).

The intrinsic rate coefficient for HOBr reacting with CP was determined at pH 6.5 (Figure 5). At this pH, approximately 99.5% of the active bromine present will be in the HOBr form. The reaction of HOBr with CP was expected to be 1–3 orders of magnitude faster than HOCl with CP. This behavior has been observed by others examining the reactivity of HOCl and HOBr with pyrene, NOM, and sulfite (14, 22, 27, 28). The reaction of HOBr with CP was essentially complete after only 10 s. The second-order rate coefficient for this reaction was determined by nonlinear regression analysis using Sigma Plot version 8.0 (Point Richmond, CA). The $k_{\text{HOBr,CP}}$ was found to be $1.14 (\pm 0.21) \times 10^9 \text{ M}^{-1} \text{h}^{-1}$ with 95% confidence intervals in parentheses, which is 3 orders of magnitude greater than HOCl oxidation of CP ($k_{\text{HOCl,CP}} = 1.72 \times 10^6 \text{ M}^{-1} \text{h}^{-1}$). Furthermore, CPO was found to be the stable transformation product in the presence of HOBr at pH 6.5. This indicates that no further oxidation of CPO occurred over a period of 6 h.

Hypobromite (OBr^-) was then investigated to determine if it reacted with either CP or CPO. Previous work found that

Table 2. Stoichiometric Equations and Rate Coefficients Used in the Chlorpyrifos Degradation Pathway Model^a

	reaction stoichiometry	rate/equilibrium coefficient (25 °C)	ref
1	$5\text{HOX} + \text{CP} \xrightarrow{k_{\text{HOX,CP}}} \text{CPO} + \text{H}^+ + \text{X}^- + \text{SO}_4^{2-}$	$k_{\text{HOBr,CP}} = 1.14 \times 10^9 \text{ M}^{-1} \text{ h}^{-1}$ $k_{\text{HOCl,CP}} = 1.72 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$	this work 10
2	$\text{CP} \xrightarrow{k_{\text{h,CP}}} \text{TCP}$	$k_{\text{h,CP}} = k_{\text{N,CP}} + k_{\text{B,CP}}[\text{OH}^-]$ $k_{\text{N,CP}} = 3.72 \times 10^{-4} \text{ h}^{-1}$ $k_{\text{B,CP}} = 37.0 \text{ M}^{-1} \text{ h}^{-1}$	23
3	$\text{CPO} \xrightarrow{k_{\text{h,CPO}}} \text{TCP}$	$k_{\text{h,CPO}} = k_{\text{N,CPO}} + k_{\text{B,CPO}}[\text{OH}^-]$ $k_{\text{N,CPO}} = 2.13 \times 10^{-3} \text{ h}^{-1}$ $k_{\text{B,CPO}} = 230 \text{ M}^{-1} \text{ h}^{-1}$	10
4	$\text{CP} + \text{OX}^- \xrightarrow{k_{\text{OX,CP}}} \text{TCP} + \text{X}^-$	$k_{\text{OBr,CP}} = 965 \text{ M}^{-1} \text{ h}^{-1}$ $k_{\text{OCl,CP}} = 990 \text{ M}^{-1} \text{ h}^{-1}$	this work 10
5	$\text{CPO} + \text{OX}^- \xrightarrow{k_{\text{OX,CPO}}} \text{TCP} + \text{X}^-$	$k_{\text{OBr,CPO}} = 1390 \text{ M}^{-1} \text{ h}^{-1}$ $k_{\text{OCl,CPO}} = 1340 \text{ M}^{-1} \text{ h}^{-1}$	this work 10
6	$\text{HOX} \rightleftharpoons \text{H}^+ + \text{OX}^-$	$\text{p}K_{\text{a}} = 8.8 \text{ (HOBr/OBr}^-)$ $\text{p}K_{\text{a}} = 7.5 \text{ (HOCl/OCl}^-)$	11 34

^a HOX represents either HOBr or HOCl; OX⁻ represents either OBr⁻ or OCl⁻.

hypochlorite (OCl⁻) acted as a supernucleophile accelerating the hydrolysis rate of both CP and CPO (i.e., chlorine-assisted hydrolysis) (10). Because CPO was found to be stable in the presence of HOBr, bromine-assisted hydrolysis experiments were conducted at pH 11, where >99% of bromine would be in the OBr⁻ form (Figure 6). The observed first-order rate of CPO loss increased linearly as bromine concentrations increased from 0 to 250 μM and the only product detected was TCP. The slope of the regression line represents the intrinsic rate coefficient for the bromine-assisted hydrolysis of CPO, $k_{\text{OBr,CPO}} = 1390 (\pm 160) \text{ M}^{-1} \text{ h}^{-1}$ with 95% confidence intervals in parentheses.

To determine if bromine also accelerates the hydrolysis of CP, the model previously developed for chlorine in buffered aqueous solutions was adopted for bromine. Because the oxidation of CP to CPO is still fast at pH values >9 due to the $\text{p}K_{\text{a}}$ of HOBr being 8.8, the model accounts for the CP oxidation by HOBr as well as CP and CPO hydrolysis pathways (eqs 5–8). Table 2 shows the elemental stoichiometric equations used to develop the following system of ordinary differential equations (ODEs). These ODEs represent a generic form of the model in which either bromine or chlorine would be the active oxidant in the system being investigated.

$$\frac{d[\text{HOX}]_{\text{T}}}{dt} = -5k_{\text{HOX,CP}}[\text{HOX}][\text{CP}] - k_{\text{OX,CP}}[\text{OX}^-][\text{CP}] - k_{\text{OX,CPO}}[\text{OX}^-][\text{CPO}] \quad (5)$$

$$\frac{d[\text{CP}]}{dt} = -k_{\text{HOX,CP}}[\text{HOX}][\text{CP}] - k_{\text{h,CP}}[\text{CP}] - k_{\text{OX,CP}}[\text{OX}^-][\text{CP}] \quad (6)$$

$$\frac{d[\text{CPO}]}{dt} = k_{\text{HOX,CP}}[\text{HOX}][\text{CP}] - k_{\text{h,CPO}}[\text{CPO}] - k_{\text{OX,CPO}}[\text{OX}^-][\text{CPO}] \quad (7)$$

$$\frac{d[\text{TCP}]}{dt} = k_{\text{h,CP}}[\text{CP}] + k_{\text{OX,CP}}[\text{OX}^-][\text{CP}] + k_{\text{h,CPO}}[\text{CPO}] + k_{\text{OX,CPO}}[\text{OX}^-][\text{CPO}] \quad (8)$$

In these equations, HOX represents either HOBr or HOCl and OX⁻ represents either OBr⁻ or OCl⁻. Scientist, an ODE

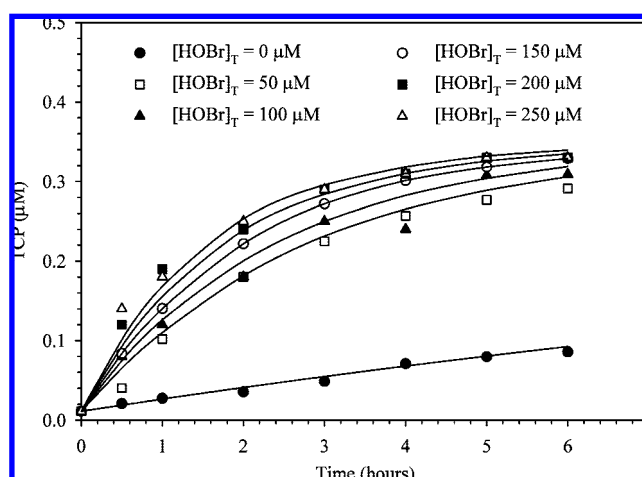


Figure 7. TCP experimental and model results for the loss of CP in the presence of bromine at pH 11. $[\text{CP}]_0 = 0.35 \mu\text{M}$, $[\text{CO}_3]_{\text{T}} = 10 \text{ mM}$, temperature = $25 \pm 1 \text{ }^\circ\text{C}$, and $[\text{HOBr}]_{\text{T}} = 0\text{--}250 \mu\text{M}$. Lines represent model results.

solver by Micromath (Salt Lake City, UT), was used to fit the bromine-assisted hydrolysis rate coefficient of CP by hypobromite ($k_{\text{OBr,CP}}$). Scientist uses a modified Powell algorithm to minimize the unweighted sum of the squares of the residual error between the predicted and experimentally observed values to estimate specific parameters in the model. Details of model development and validation have previously been discussed (10).

To determine $k_{\text{OBr,CP}}$, a pooled data set at pH 11 was collected in which both CPO and TCP concentrations were used to determine the hypobromite-assisted hydrolysis rate coefficient. Figure 7 shows the experimental and model results fitting $k_{\text{OBr,CP}}$ over the $[\text{HOBr}]_{\text{T}}$ concentration range of 0–250 μM. The loss of CP proceeded more rapidly at pH 11 in the presence of bromine than chlorine (10). Although approximately only 0.6% of bromine present was in the HOBr form, up to one-third of the initial CP concentration was transformed to CPO within the first hour of the experiment, which was 7 times greater than in the presence of chlorine when 0.03% was in the HOCl form at pH 11. This explains the rapid loss of CP and TCP formation in the presence of bromine because the oxidation rate is more rapid than with chlorine. Using the model, $k_{\text{OBr,CP}}$ for CP was

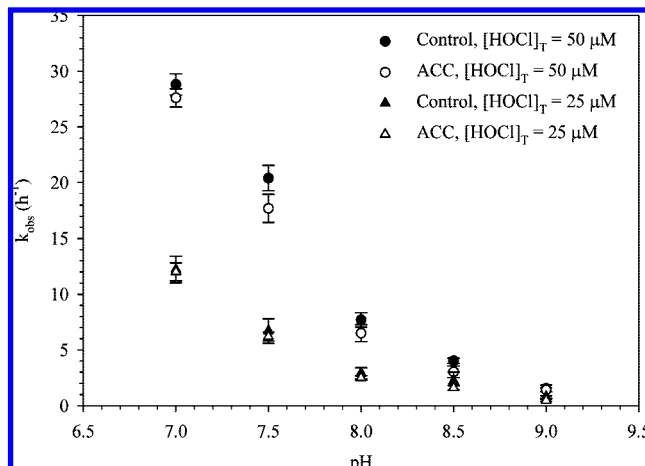


Figure 8. Observed first-order loss rates of CP over the pH range of 7.0–9.0 with and without ACC present. $[CP]_0 = 0.5 \mu\text{M}$, $[HOCl]_T = 25$ and $50 \mu\text{M}$, $[\text{buffer}]_T = 10 \text{ mM}$, $[\text{ACC}] = 1.61 \text{ mg of C/L}$, and temperature = $25 \pm 1 \text{ }^\circ\text{C}$. Error bars represent 95% confidence intervals.

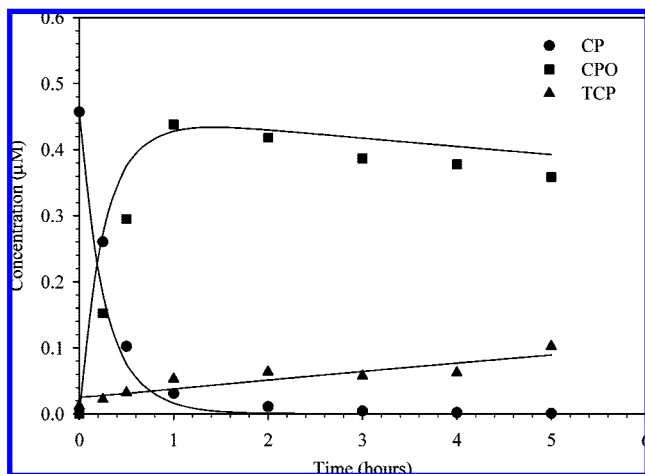


Figure 9. Transformation of CP to CPO and degradation of CPO in the presence of free chlorine at pH 9.0. $[CP]_0 = 0.45 \mu\text{M}$, $[HOCl]_T = 50 \mu\text{M}$, $[\text{CO}_3]_T = 10 \text{ mM}$, and temperature = $25 \pm 1 \text{ }^\circ\text{C}$. Lines represent model results.

$965 (\pm 110) \text{ M}^{-1} \text{ h}^{-1}$ with 95% confidence intervals in parentheses. Using nonlinear regression analysis and established reaction pathways allowed for the parametrization of $k_{\text{OBr}^-, \text{CP}}$ in this complicated yet well-defined reaction system.

The bromine-assisted hydrolysis rate coefficients for both CP and CPO were found to be very similar to those found for chlorine (Table 2). This result was unexpected because the transformation of CP to CPO by HOBr was significantly greater than for HOCl over the pH range of 6.5–9. With the halogen-assisted hydrolysis (XO^-) of CP and CPO, the importance of the alpha effect for nucleophilic attack at the tetrahedral phosphorus atom strongly depends on the lone pairs of electrons on the halogen atom (i.e., Cl or Br). Previous work investigating the nucleophilicity of OCl^- , repulsions between the lone pairs of electrons on the chlorine atom and the oxygen atom were found to enhance the nucleophilicity of hypochlorite toward tetrahedral phosphorus moieties (29). Because of these repulsions, OCl^- satisfies the criteria to be considered a supernucleophile (30). The molecular structures of hypochlorite and hypobromite are similar and the electronegativities of bromine (2.96) and chlorine (3.16) are not significantly different, the alpha effect appears to apply to OBr^- as well. However, few

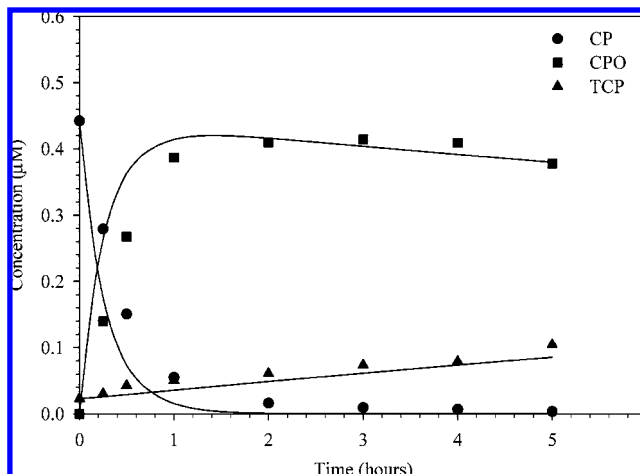


Figure 10. Transformation of CP to CPO and degradation of CPO in the presence of free chlorine at pH 8.5. $[CP]_0 = 0.44 \mu\text{M}$, $[HOCl]_T = 25 \mu\text{M}$, $[\text{ACC}] = 1.1 \text{ mg of C/L}$, $[\text{CO}_3]_T = 10 \text{ mM}$, and temperature = $25 \pm 1 \text{ }^\circ\text{C}$. Lines represent model results.

studies exist in the literature examining why halogenated oxidants act as nucleophiles. Future work is planned to further investigate the alpha effect of these oxidants with additional OP pesticides in order to gain greater insight into this phenomenon.

Modeling CP Transformation in the Presence of Chlorine

and Bromide. With the intrinsic rate coefficients for HOBr and OBr^- with CP and CPO known, an attempt was made to model the chlorine/bromide/CP system. The current model assumes that for the loss of 1 mol of CP there is a subsequent loss of 5 mol of either bromine or chlorine. This assumes that regardless of either oxidant being present, the sulfur that is lost from the parent OP is instantaneously converted to sulfate (SO_4^{2-}) due to the overwhelming oxidant concentration. However, the chlorine/bromide system produces HOCl, HOBr, and BrCl as three powerful oxidants not only transforming CP to CPO but competing to oxidize the sulfur from CP to sulfate. Because the affinities for the three separate oxidants with each sulfur species (S, SO, SO_2 , SO_3^{2-}) could not be found in literature, attempts at modeling this system with a mechanistic approach were unsuccessful.

Chlorination of CP in the Presence of NOM. The presence of NOM could potentially decrease the rate of CP degradation by acting as a sink for oxidants used in drinking water treatment. Conventional physical–chemical water treatment processes such as coagulation and lime softening remove a portion of the hydrophobic fraction of the NOM (31, 32). More advanced water treatment processes such as granular activated carbon (GAC) or membrane filtration are capable of removing additional NOM fractions (33). However, few community water systems employ these more advanced technologies. For example, these processes are not employed at the ACC plant. Therefore, only a portion of the hydrophobic NOM fraction will be removed. Chlorine demand studies were conducted over the pH range of 7–9 on the ACC water to determine chlorine consumption as a function of time. Over the first 0.5 h, approximately $6 \mu\text{M}$ of the free chlorine initially present ($[HOCl]_T = 25$ and $50 \mu\text{M}$) was consumed by the NOM in a multiphasic reaction and was found not to be dependent on pH. After the initial chlorine demand of the NOM was satisfied, the loss of free chlorine attributable to reaction with NOM was relatively slow ($k_{\text{obs}} = 0.012 \text{ h}^{-1}$) over the pH range of 7–9. This suggests that the

NOM present in the ACC water may affect the rate of CP transformation because chlorine demand is consistent over the pH range of 7–9.

To examine the effect of NOM on the transformation of CP, experiments were conducted over the pH range of 7–9 and in the presence of 25 and 50 μM free chlorine. **Figure 8** shows the observed first-order rate of CP loss with and without the presence of NOM. In the presence of ACC NOM, the observed loss of CP was very similar to, if not exactly the same as, the control experiments. It appears that the conventional treatment performed at the ACC plant removed a portion of the hydrophobic NOM fraction that is usually associated with significant chlorine demand (20). Therefore, it might be possible for the current model (developed with experiments in laboratory water: eqs 5–8) to accurately predict the transformation of CP in this low humic water.

Indeed, model results were found to adequately predict the loss of CP in the presence of ACC water. The ACC water does contain bromide at 0.15 μM , but this low bromide concentration was not expected to significantly affect the rate of CP transformation (**Figures 2 and 3**). The model performed very well, predicting the formation and stability of CPO, the more toxic transformation product, as well as TCP. At pH values >8 , CPO becomes susceptible to chlorine-assisted hydrolysis due to the greater abundance of the hypochlorite ion. The model not only predicted CPO formation but also showed that CPO was slowly being transformed to TCP over the course of the experiment (**Figures 9 and 10**). This appears to validate the ability of the model to adequately predict the loss of CP in the presence of free chlorine and NOM, as well as the ability of the model to predict the formation and stability of CPO in the presence of free chlorine. However, additional model validation studies in the presence of different source waters are warranted.

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