Published in final edited form as:

Chemosphere. 2013 September ; 92(11): 1417–1422. doi:10.1016/j.chemosphere.2013.03.045.

Kinetic study of the reactions between chloramine disinfectants and hydrogen peroxide: Temperature dependence and reaction mechanism

Garrett McKay^a, Brittney Sjelin^a, Matthew Chagnon^a, Kenneth P. Ishida^b, and Stephen P. Mezyk^{a,*}

^aDepartment of Chemistry and Biochemistry, California State University at Long Beach, 1250 N. Bellflower Blvd., Long Beach, CA 90804, United States

^bResearch and Development Department, Orange County Water District, Fountain Valley, CA 92708, United States

Abstract

The temperature-dependent kinetics for the reaction between hydrogen peroxide and chloramine water disinfectants (NH_2Cl , NHCl_2 , and NCl_3) have been determined using stopped flow-UV/Vis spectrophotometry. Rate constants for the mono- and dichloramine-peroxide reaction were on the order of $10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, respectively. The reaction of trichloramine with peroxide was negligibly slow compared to its thermal and photolytically-induced decomposition. Arrhenius expressions of $\ln(k_{\text{H}_2\text{O}_2-\text{NH}_2\text{Cl}}) = (17.3 \pm 1.5) - (51500 \pm 3700)/RT$ and $\ln(k_{\text{H}_2\text{O}_2-\text{NHCl}_2}) = (18.2 \pm 1.9) - (75800 \pm 5100)/RT$ were obtained for the mono- and dichloramine peroxide reaction over the temperature ranges 11.4–37.9 and 35.0–55.0 °C, respectively. Both monochloramine and hydrogen peroxide were first-order in the rate-limiting kinetic step and concomitant measurements made using a chloride ion selective electrode showed that the chloride was produced quantitatively. These data will aid water utilities in predicting chloramine concentrations (and thus disinfection potential) throughout the water distribution system.

GRAPHICAL ABSTRACT

*Corresponding author. Tel.: +1 562 985 4649., Stephen.Mezyk@csulb.edu (S.P. Mezyk).

Keywords

Chloramines; Chloramination; Water disinfection; Hydrogen peroxide; Kinetics

1. Introduction

The chemical disinfection of drinking water and wastewater is of primary importance as it is the final treatment step before human consumption (CDPH, 2012) and most water reuse applications (CRWQCB, 2002). While the addition of chlorine has been utilized to disinfect drinking water for over a hundred years, its use can also lead to the formation of toxic, low molecular weight, halogenated disinfection byproducts (DBPs) (Rook, 1974; Golfinopoulos and Nikolaou, 2005; Krasner et al., 2006; Richardson et al., 2007; Goslan et al., 2009; Krasner, 2009; Krasner et al., 2009a,b). Therefore, over the past few decades chloramines have gained favor as an alternative form of water disinfection due to the lower production of trihalomethanes (THMs) and haloacetic acids (HAAs) and longer residence time in the water distribution system. (EPA, 1999; Diehl et al., 2000; Vikesland et al., 2001; Hua and Reckhow, 2007). Chloramines are produced by adding ammonia to chlorine-treated waters at a time that allows for maximum microbial inhibition with minimum DBP formation (Carlson and Hardy, 1988; Hua and Reckhow, 2007). Monochloramine (NH_2Cl) can be present in post-treated water at concentrations up to 2–2.5 mg L^{-1} (as equivalent Cl_2) (Johnson et al., 2002).

Chloramine addition is also used in large-scale wastewater treatment for indirect potable reuse. For example, in the Advanced Water Purification Facility (AWPF) at the Orange County Water District (OCWD) Fountain Valley, CA, USA chloramine is generated through chlorine (hypochlorite) addition to partially-nitrified secondary wastewater effluent prior to microfiltration to prevent biofouling of reverse osmosis (RO) membrane systems. Addition of chlorine to other OCWD tertiary effluent also allows non-potable recycling of this water (purple pipe water) for irrigation purposes (CRWQCB, 2002). However, the chemistry of chloramines with various components of treated wastewater is not completely understood. In addition, the long residence time of chloramine can also impact further water treatment; for

example, the OCWD AWPf's treatment of RO permeate using an advanced oxidation process (AOP) prior to indirect potable reuse. AOPs are characterized by the production of hydroxyl radical ($\text{HO}^\bullet$), which is most commonly produced using $\text{H}_2\text{O}_2/\text{UV}$ irradiation or $\text{H}_2\text{O}_2/\text{O}_3$ mixtures (von Gunten, 2003; von Sonntag, 2006; von Gunten, 2007; Wert et al., 2009, 2010). The subsequent reaction of $\text{HO}^\bullet$ with monochloramine occurs quickly, $k = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, (Poskrebyshev et al., 2003), and this radical scavenging pathway could significantly impact the efficiency of the AOP in removing residual chemical contaminants. Photolytic decomposition (Cooper et al., 2007; Watts and Linden, 2007; De Latt et al., 2010; Li and Blatchley, 2009) of these chloramines would also impact the overall AOP efficiency.

Moreover, a portion of the OCWD AWPf AOP-treated recycled water is piped 13 miles over a 12 h period before ultimate release for aquifer recharge. Since only a small fraction of the added hydrogen peroxide in the AOP is converted to $\text{HO}^\bullet$ radicals, there is always some residual peroxide ($\sim 2.4 \text{ mg L}^{-1}$) that could react with remaining chloramines. This chemistry could impact the subsequent formation of DBPs in the discharge pipeline. For example, in basic pH waters monochloramine can also form hydroxylamine (NH_2OH) a compound that is a suspect mutagen that targets the blood and nervous system (EPA, 2010). In addition, chloramination of trace organics and recalcitrant natural organic matter has been shown to produce N-nitrosodimethylamine (NDMA) and other DBPs (Wan et al., 2013; Hatt et al., 2013; Mitch and Sedlak, 2002). The eventual fate of residual chloramines could also be further complicated by their additional speciation that occurs in slightly acidic waters. A recent measurement of source waters from OCWD's AWPf showed all three chloramines (mono-, di-, and tri-chloramine, assumed to be in equilibrium) were present in their RO permeate at a pH of 5.5:

in the approximate ratio 48%:50%:2%, which is consistent with what is expected at this pH (Palin, 1950).

Despite these concerns, the kinetics, Arrhenius parameters, and mechanism of the reaction between hydrogen peroxide and chloramines have not been reported. Therefore, in this study, we have directly measured the temperature-dependent rate constants for the reaction of monochloramine ($k_{\text{H}_2\text{O}_2-\text{NH}_2\text{Cl}}$) and dichloramine ($k_{\text{H}_2\text{O}_2-\text{NHCl}_2}$) with hydrogen peroxide:

In addition, chloride ion sensitive electrode (Cl-ISE) experiments have been performed to determine and quantify reaction products. These data will help improve the understanding of

chloramine decomposition in water distribution systems (Valentine et al., 1986; Leung and Valentine, 1994; Vikesland et al., 2001).

2. Materials and methods

2.1. Chemicals and peroxide standardization

Hydrogen peroxide (~30% solution) was purchased from Sigma Aldrich, potassium permanganate, ammonium chloride, sodium chloride, and sodium nitrate were from VWR, and sodium tetraborate decahydrate and sodium hypochlorite (5.65–6%) were from Fisher Scientific. All compounds were >99% purity. Solutions were prepared in Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$). The peroxide solution was standardized using permanganate titration with glassware that had been passivated in ~35% sulfuric acid for at least 1 h.

2.2. Chloramine preparation

Monochloramine was produced in 2.00 mM sodium tetraborate decahydrate buffer (pH 8.8 ± 0.1) by adding 20.0 mL of $6.25 \times 10^{-3} \text{ M}$ NaOCl dropwise to 5.00 mL of $2.5 \times 10^{-2} \text{ M}$ NH_4Cl with vigorous stirring over a period of about 1 h in the dark (Jafvert and Valentine, 1992):

The solution was stirred for an additional 30 min after complete NaOCl addition. Dichloramine was prepared by adjusting prepared monochloramine solutions to pH 3.4 using perchloric acid. The pH was continuously adjusted until stable (constant to 0.01 pH units over a 10-min period). Trichloramine was produced by mixing sodium hypochlorite and ammonium chloride, both adjusted to pH 3.6 ± 0.1 , in a 3:1 ratio. Following this mixing, the trichloramine solution was kept in a completely filled flask and stored in the dark overnight in order for any side reactions to go to completion (Yiin and Margerum, 1989).

All chloramine species were identified and quantified spectrophotometrically using an Ocean Optics (Red Tide, USB 650) or Shimadzu (UV-1601) UV/Vis spectrophotometer. The extinction coefficients used in this study for the three species are listed in Table S1 (Yiin and Margerum, 1989). Fresh chloramine solutions were prepared daily, used immediately at their standard pH's, and were found to thermally decay less than ~10% over a 10-h period.

2.3. Kinetic experiments

Most kinetic experiments were performed under pseudo-first-order conditions using excess peroxide (greater than 20:1 $[\text{H}_2\text{O}_2]:[\text{-chloramine}]$). Peroxide concentrations were diluted from the standardized stock adjusted to match the pH of the chloramine solution (8.8 for NH_2Cl , 3.4 for NHCl_2 , and 3.6 for NCl_3) so that the pH of the reaction mixture was the same as the initial chloramine solution. A Hi-Tech Scientific 61DX2 stopped-flow system was used to measure monochloramine–peroxide kinetics at a wavelength of 284 nm. Blank scans for each of these components showed no significant monochloramine or hydrogen peroxide loss over the timescale of these experiments (see Fig. S1).

However, within the measurement cuvette in the stopped-flow spectrophotometer, where the solution was constantly illuminated at deep-UV wavelengths, significant absorbance decreases for both di- and trichloramine were observed. Chloramines have been shown to be susceptible to photolysis at 254 nm ($\Phi_{\text{NH}_2\text{Cl}, 253.7\text{nm}} = 0.26\text{--}0.62 \text{ mol E}^{-1}$ and $\Phi_{\text{NHCl}_2, 253.7\text{nm}} = 0.82\text{--}1.8 \text{ mol E}^{-1}$) (Cooper et al., 2007; Watts and Linden, 2007; De Latt et al., 2010; Li and Blatchley, 2009). Quantum yields at 282 nm ($\Phi_{\text{NH}_2\text{Cl}, 282\text{nm}} = 0.21 \text{ mol E}^{-1}$; $\Phi_{\text{NHCl}_2, 282\text{nm}} = 2.25 \text{ mol E}^{-1}$; $\Phi_{\text{NCl}_3, 282\text{nm}} = 9.50 \text{ mol E}^{-1}$) (Li and Blatchley, 2009) are more significant for di- and tri- than monochloramine. For this reason, di- and trichloramine–peroxide reaction kinetics were measured by taking individual grab samples from a sealed, dark, reaction container containing minimal head space. Changes in the concentration of di- and trichloramine were monitored from absorption changes at 294 and 336 nm, respectively. Following this methodology control experiments showed <10% decrease in absorbance of dichloramine at 50 °C over the timescale of these experiments. Unfortunately, similar experiments for trichloramine still showed significant decreases in absorbance (see Fig S2).

A Symphony combination chloride electrode (VWR) was used for all chloride ion selective electrode (Cl-ISE) experiments. The Cl-ISE was calibrated daily using sodium chloride standards and slopes for the calibration were always within 10% of the theoretical value. To eliminate electrode drift when the Cl-ISE was used in chloramine/hydrogen peroxide solutions the Cl-ISE was kept in the chloramine solution until the reading stabilized (about 5 min), at which point the stock hydrogen peroxide solution was injected. The potentials of the sodium chloride standards were re-checked after the completed experiment and deviated from the original calibration by less than 10%.

3. Results and discussion

3.1. Monochloramine–H₂O₂ temperature-dependent rate constant measurements

The overall stoichiometric equation for the redox reaction of monochloramine with hydrogen peroxide is:

This is clearly a multi-step reaction. To establish the stoichiometry of the rate-limiting step in the overall reaction sequence, initial-rate measurements as a function of both monochloramine and hydrogen peroxide concentration were performed. These data are shown in Fig. 1a, and demonstrate that the rate-limiting step is first-order in both; with slopes of 1.03 ± 0.03 and 0.92 ± 0.10 for monochloramine and hydrogen peroxide, respectively. This gives the overall rate expression as:

$$-d[\text{NH}_2\text{Cl}]/dt = k_{\text{H}_2\text{O}_2\text{--NH}_2\text{Cl}} [\text{H}_2\text{O}_2][\text{NH}_2\text{Cl}] \quad (6)$$

Typical kinetic decay data as monitored by absorbance change at 284 nm are shown in Fig. 1b for the decay of monochloramine at 37.9 °C. While both hydrogen peroxide and monochloramine absorb at this wavelength, the molar absorptivity of monochloramine

($\epsilon_{284\text{nm}} = 40.5 \text{ M}^{-1} \text{ cm}^{-1}$) is much greater than that of peroxide ($\epsilon_{284\text{nm}} = 3.0 \text{ M}^{-1} \text{ cm}^{-1}$) (see Fig. S3 and Table S1). Under these conditions, the decay of the monochloramine absorbance followed excellent first-order kinetics, and were fitted using a single exponential decay equation:

$$Abs = Abs_o e^{-k' t} + B \quad (7)$$

where Abs is the measured absorbance at time t , Abs_o is the initial absorbance, k' is pseudo-first-order rate constant, and B is the limiting baseline absorbance. At 37.9°C a plot of fitted k' values against hydrogen peroxide concentration (Fig. 1c) gave a second order rate constant of $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}} = (7.72 \pm 0.19) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.

A summary of all the temperature-dependent $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}}$ rate constants measured in this study for monochloramine and hydrogen peroxide is given in Table 1. These data also follow excellent Arrhenius behavior (see Fig. 2a), with a temperature-dependent rate constant expression being:

$$\ln(k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}}) = (17.3 \pm 1.5) - (51,500 \pm 3700)/RT$$

corresponding to an activation energy of $51.5 \pm 3.7 \text{ kJ mol}^{-1}$. (8)

corresponding to an activation energy of $51.5 \pm 3.7 \text{ kJ mol}^{-1}$.

Concomitant kinetic measurements using a Cl-ISE to quantify the chloride production were also performed in this study, with typical data shown for $\text{NH}_2\text{Cl-H}_2\text{O}_2$ reaction at 23.8°C shown in Fig. 3. As with monochloramine-peroxide decay, these data fit excellently to first-order kinetics, this time using the exponential growth expression:

$$[\text{Cl}^-] = [\text{Cl}^-]_o (1 - e^{-k'_9 t}) + B \quad (9)$$

where $[\text{Cl}^-]_o$ is the concentration of chloride produced in the reaction, k'_9 is the pseudo-first-order rate constant, and B is the baseline adjustment corresponding to the initial chloride concentration based on the slight excess of NH_4Cl used. At this temperature, the rate constant obtained was k'_9 of $5.23 \times 10^{-3} \text{ s}^{-1}$, corresponding to the second order rate constant $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}} = (2.86 \pm 0.02) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. The corresponding $[\text{Cl}^-]_o$ calculated value was $1.87 \pm 0.01 \text{ mM}$. This measured rate constant is in very good agreement with that obtained using stopped flow absorption kinetics $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}} = (2.76 \pm 0.13 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 24.6°C) and the determined chloride concentration correlates well with the initial concentration of monochloramine used (1.98 mM).

3.2. Dichloramine-peroxide temperature-dependent rate constant measurements

The redox reaction between dichloramine and hydrogen peroxide proceeds according to the stoichiometry:

Spectrophotometry grab-sample kinetic decay experiments for this reaction were performed using the NHCl_2 absorbance maximum at 294 nm, over the temperature range 35–55 °C. These data are also summarized in Table 1, and shown as the Arrhenius plot in Fig. 2b. Kinetic experiments were attempted at lower temperatures; however, these data had significant error due to interfering photolytic and thermal dichloramine loss at longer times. The NHCl_2 values were much slower than measured for NH_2Cl , ranging from $k_{\text{H}_2\text{O}_2\text{-NHCl}_2} = 1.14\text{--}6.69 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ over this temperature range. The Arrhenius expression for these data was:

$$\ln(k_{\text{H}_2\text{O}_2\text{-NHCl}_2}) = (18.2 \pm 1.9) - (75,800 \pm 5100)/RT \quad (11)$$

corresponding to an activation energy $75.8 \pm 5.1 \text{ kJ mol}^{-1}$. Based on this expression, an extrapolated room temperature value of $k_{\text{H}_2\text{O}_2\text{-NHCl}_2}$ was $3.60 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ at 23.5 °C.

Chloride ion-selective electrode experiments were also performed for the dichloramine–peroxide reaction, and while good qualitative agreement in both the kinetic values and total chloride yield were obtained, the larger potential drift encountered for the longer times required made quantitative time-dependent measurements challenging.

These markedly slower rate constants suggest that dichloramine is a stronger oxidant than monochloramine, consistent with reported redox potentials for these two compounds of 311 and 320 mV, respectively (Victorin et al., 1972). As such, dichloramine in water distribution systems would be less impacted than that of monochloramine by the presence of excess peroxide. Dichloramine is known to be a more effective biocide than monochloramine (White, 2010), and is more stable below pH 6 (Palin, 1950), but its formation is usually avoided since more chlorine is consumed and its presence can affect both taste and odor.

3.3. Trichloramine–peroxide rate constant measurements

Since trichloramine has a high vapor pressure and is very light sensitive, its reactivity with hydrogen peroxide was measured as for dichloramine. The absorbance decay observed for this reaction was determined at 40 °C. However, this pseudo-first-order decay was found to be almost identical to that for the control experiment of only trichloramine in water (Fig. S2, $k' = 2.0 \times 10^{-4} \text{ s}^{-1}$), indicating that reaction between trichloramine and hydrogen peroxide is even slower than that for dichloramine, and negligibly slow compared to its loss due to vaporization or photolysis. Therefore no other quantitative measurements of the $\text{NCl}_3\text{--H}_2\text{O}_2$ rate constants were performed in this study.

3.4. Reaction mechanism

The very close agreement between the absorbance and Cl-ISE measurements for monochloramine–peroxide reaction suggests that the rate-limiting step involves the loss of chloride in the first step in a multi-step reaction sequence:

Based on the electronic structure of both reactants, it is proposed that an $\text{S}_{\text{N}}2$ type mechanism occurs in this step, with monochloramine acting as the electrophile and peroxide as the nucleophile (Scheme 1). Although the reactivity of the chloramine electrophile might be expected to increase for di- and trichloramine, we attribute the measured slower reactivity to the positive charge forming on the peroxide oxygen being inductively destabilized by the additional chlorines. This could also explain the larger activation energy of the dichloramine reaction compared to monochloramine. In addition, the extra chlorine atom may provide additional steric hindrance for the dichloramine reaction, though the Arrhenius prefactors for each reaction were the same within error.

Another possible explanation for the difference in activation energies is that the monochloramine–peroxide reaction is undergoing general base catalysis, which is not possible for the dichloramine–peroxide reaction since the latter is under more acidic conditions. Hydroxide-mediated general base catalysis can occur in the addition of hydrogen peroxide to some carbonyl compounds (Jencks, 1972). To investigate this possibility, we measured $k_{\text{H}_2\text{O}_2-\text{NH}_2\text{Cl}}$ over the pH range 8.4–9.1 at 34.0 °C. This range was chosen to prevent monochloramine speciation (at pH less than 8.4) and prevent hydroxyl amine formation (at pH greater than 9.1). Second-order $k_{\text{NH}_2\text{Cl}-\text{H}_2\text{O}_2}$ values of 5.69 (± 0.06), 5.71 (± 0.01), 5.73 (± 0.1), and 5.67 (± 0.01) $\text{M}^{-1} \text{ s}^{-1}$ were obtained at pH values of 8.4, 8.6, 8.8, and 9.1, respectively, and these consistent data suggests that general base catalysis is not occurring over pH 8.4–9.1. The pH dependence of the dichloramine–peroxide reaction was not investigated due to the rapid re-speciation that occurs for dichloramine with change in pH (Mezyk et al., in preparation).

The observed decrease in reactivity for the chloramine–peroxide reaction is also consistent both experimental (Roberts et al., 1992) and theoretical (Shaik, 1983) models of $\text{S}_{\text{N}}2$ reactivity of halomethanes. More specifically, in the former study, the reaction between CH_2BrCl with HS^- proceeded slower than that of CH_2Br_2 , suggesting that steric hindrance of the electrophile decreases the reactivity. Furthermore, the reactivity of CH_2Cl_2 with HS^- was even slower than that of CH_2Br_2 and CH_2BrCl , indicating that both steric and electronic factors are influencing the rate. The reaction between chloramines and peroxide also agree with Shaik's model of $\text{S}_{\text{N}}2$ reactivity (Shaik, 1983) in which the presence of α -halo substituents (beside the leaving group) decrease reactivity. Moreover, the reactivity is further decreased when the α -halo substituent is the same as the leaving group, which is the case for dichloramine.

3.5. Chloramine decay modeling

Assuming the measured OCWD distribution of chloramines at pH 5.5, with a total residual 1.5 mg L^{-1} chlorine plus 2.4 mg L^{-1} H_2O_2 in the final product water, the time-dependent variation of all species over the 12 h discharge pipeline period can be calculated at 25 °C using the simple kinetic model summarized in Table 2 and also allowing for the 3:1 H_2O_2 :chloramine stoichiometry involved. The results of these calculations are shown in Fig.

4. For this model the $k_{\text{H}_2\text{O}_2\text{-NCl}_3}$ rate constant was corrected to a 25 °C value of $k_{\text{NCl}_3} = 2.88 \times 10^{-5} \text{ s}^{-1}$, assuming an activation energy of 100 kJ mol^{-1} . However, the negligibly small initial concentration ($2.33 \times 10^{-7} \text{ M}$) and slow reaction rate constant for reaction meant that it did not have any significant impact on the overall chloramine chemistry. The calculated data show that over this time period, about 2/3 of the initial monochloramine and trichloramine concentration was removed, as was 20% of NHCl_2 , but only negligible change (<5%) in the residual H_2O_2 concentration occurred. There may be additional chemistry that occurs between chloramines and other components of the water matrix that could also impact the chloramine decay chemistry.

4. Conclusions

1. Temperature-dependent rate constants have been measured for the reaction of hydrogen peroxide with mono- and dichloramine in aqueous solution. Initial rate studies revealed that the reaction between monochloramine and peroxide was first order in both reactants. The reaction of trichloramine with peroxide was found to be negligibly slow compared to its thermal- and photolytically-induced decomposition. The chloramine reactivity decreased with increasing number of attached chlorine atoms, with $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}}$ and $k_{\text{H}_2\text{O}_2\text{-NHCl}_2}$ values on the order of 10^{-2} and $10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at room temperature, respectively. Arrhenius behavior was obtained for mono- and dichloramine peroxide reaction with calculated activation energies of 51.5 ± 3.7 and $75.8 \pm 5.1 \text{ kJ mol}^{-1}$, respectively.
2. The rate of chloride production was equal to the rate of chloramine loss, suggesting that elimination of chloride is involved in the rate limiting step. Furthermore, the production of chloride was quantitative, further suggesting that chloride is the initial product from the reaction. Based on this a mechanism is proposed in which the peroxide nucleophile reactions with the nitrogen atom of the chloramine electrophile.
3. Kinetic modeling of chloramine concentrations show a 66% loss of monochloramine and 20% loss of dichloramine, which could affect the disinfection potential of chloramines in the water distribution system and subsequent human consumption and potentially impact the lifespan of OCWD's 13-mile concrete pipeline.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We would like to thank the OCWD for partial funding of this research. G.M. thanks the CSULB Department of Chemistry and Biochemistry for funding through the Michael Monahan Research Fellowship. M.C. thanks the Research Initiative for Science Enhancement (RISE) (Grant # 5R25GM071638-08) program for support. We would also like to thank P.T. Buonora and K. Slowinska for helpful discussions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.03.045>.

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HIGHLIGHTS

- Decay of chloramine water disinfectants through reaction of H_2O_2 was investigated.
- Chloramine- H_2O_2 reactivity decreases with increasing chlorine substitution.
- Monochloramine's reaction with H_2O_2 results in quantitative chloride production.
- Arrhenius parameters for mono- and dichloramine reactions are determined.
- Kinetic modeling shows a 66% loss of monochloramine over a 12 h period.

Fig. 1.

(a) Initial rates plot for monochloramine (red, $\square$) and hydrogen peroxide (blue, $\circ$). Data points represent the log of the initial rate which was determined from a linear fit of the initial portion of the exponential pseudo-first-order decay of NH_2Cl at 24.3 °C in 2 mM sodium tetraborate buffer ($\text{pH } 8.8 \pm 0.1$). Solid line corresponds to a weighted linear fit with a slope of (a) 1.03 ± 0.03 ($R^2 = 0.998$), and (b) 0.92 ± 0.10 ($R^2 = 0.977$) which indicates that the reaction is first order with respect to both monochloramine and peroxide. (b) Pseudo-first-order decay kinetics measured at 284 nm for the reaction of monochloramine and hydrogen peroxide at 37.9 °C in 2 mM sodium tetraborate buffer ($\text{pH } 8.8 \pm 0.1$). Kinetic traces were obtained using a Hi-Tech Scientific Instruments 61DX2 Stopped Flow system at peroxide concentrations of 62 (∇), 82 ($\diamond$), 102 (Δ), 123 ($\circ$), and 144 mM ($\square$). Data are offset to aid visibility. Solid lines are fitted exponential decay kinetics with corresponding rate constants of $4.82, 6.39, 7.89, 9.72$, and $11.1 \times 10^{-3} \text{ s}^{-1}$, respectively. Errors from the fitted pseudo-first-order curves were less than one percent. (c) Pseudo-first-order plots for the reaction between monochloramine and peroxide at 11.2 ($\square$), 17.5 ($\circ$), 24.6 (Δ), 30.4 ($\diamond$), and 37.9 (∇) °C. The value of $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}}$ for 37.9 °C (∇) as described in a) is $k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}} = (7.72 \pm 0.19) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2.

Arrhenius plot for the reaction between (a) monochloramine and peroxide over the temperature range 11.2–37.9 °C. Solid line corresponds to a weighted linear fit ($R^2 = 0.985$), with an Arrhenius expression of $\ln(k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}}) = (17.3 \pm 1.5) - (51500 \pm 3700)/RT$. Arrhenius plot for the reaction between (b) dichloramine and peroxide over 35.0–55.0 °C. Solid line corresponds to a weighted linear fit ($R^2 = 0.982$), with an Arrhenius expression of $\ln(k_{\text{H}_2\text{O}_2\text{-NHCl}_2}) = (18.2 \pm 1.9) - (75800 \pm 5100)/RT$.

Fig. 3.

Pseudo-first-order growth of chloride concentration as monitored by Cl-ISE at 23.8 °C upon injection of 800 μL of 9.69 M H_2O_2 (experimental $[\text{H}_2\text{O}_2] = 0.183 \text{ M}$) to 40 mL of NH_2Cl in 2 mM sodium tetraborate buffer ($\text{pH } 8.8 \pm 0.1$). The line corresponds to a fit of the data using a first-order growth model ($R^2 = 0.999$) with a corresponding chloride production rate constant of $k'_g = 5.23 \times 10^{-3} \text{ s}^{-1}$. Individual data point error bars correspond to a single standard deviation based on triplicate trials. Inset is typical calibration curve for the Cl-ISE. Weighted line corresponds to a linear fit of the data ($R^2 = 0.999$) (potential = $-57.0 \times \log[\text{Cl}^-] - 93.35$).

Fig. 4. Calculated loss of residual H₂O₂ (Δ), monochloramine ($\square$) and dichloramine ($\circ$) over a 12-h period after OCWD MF/RO/UV-H₂O₂ wastewater treatment.

Scheme 1.

Proposed mechanism for the initial step of the reaction between monochloramine and hydrogen peroxide.

Table 1

Temperature-dependent rate constants, activation energies, and prefactors for the reaction of mono- (2 mM sodium tetraborate buffer, pH 8.8 ± 0.1) and dichloramine (2 mM sodium tetraborate buffer, pH 3.4 ± 0.1) with hydrogen peroxide.

Temp. (°C)	$k_{\text{H}_2\text{O}_2\text{-NH}_2\text{Cl}} (\text{M}^{-1} \text{s}^{-1}) \times 10^2$	Temp. (°C)	$k_{\text{H}_2\text{O}_2\text{-NHCl}_2} (\text{M}^{-1} \text{s}^{-1}) \times 10^5$
11.2	1.27 ± 0.16	35.0	1.14 ± 0.14
17.5	1.77 ± 0.14	40.0	2.05 ± 0.04
		44.0	2.66 ± 0.30
24.6	2.76 ± 0.13	45.0	2.79 ± 0.39
30.4	5.06 ± 0.10	50.0	4.84 ± 0.05
37.9	7.72 ± 0.19	55.0	6.69 ± 0.44
Species	ln (A)		E_a (kJ mol ⁻¹)
NH ₂ Cl	17.3 ± 1.5		51.5 ± 3.7
NHCl ₂	18.2 ± 1.9		75.8 ± 5.1

Table 2

Monochloramine decay model including peroxide reactions (all rate constants from the literature are at room temperature, those for our work are given in the text).

Reaction	Rate constant	Reference
$\text{NH}_2\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{products}$	$2.76 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{products}$	$2.11 \times 10^{-5} \text{ s}^{-1}$	Morris and Isaac (1981)
$\text{NHCl}_2 + \text{H}_2\text{O}_2 \rightarrow \text{products}$	$3.60 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$	This work
$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{products}$	$6.39 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$	Margerum et al. (1978)
$\text{NCl}_3 \rightarrow \text{products}$	$2.88 \times 10^{-5} \text{ s}^{-1}$	This work