

# Stability of Cyanogen Chloride in the Presence of Free Chlorine and Monochloramine

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Cyanogen chloride (CNCl) is a disinfection byproduct found in chlorinated and chloraminated drinking water. Although there is an apparent greater association of CNCl with chloraminated water relative to chlorination systems, it was not clear whether these phenomenological observations are explained by differences in the stability or formation potentials of CNCl between the two disinfectants. In this study, the stability of CNCl was examined in the presence of free chlorine and monochloramine using membrane introduction mass spectrometry. CNCl decomposes relatively rapidly when free chlorine is present but is stable in the presence of monochloramine. The decomposition kinetics and observed reaction products are consistent with a hypochlorite-catalyzed hydrolysis mechanism, and the rate law is described by  $(d[\text{CNCl}]/dt) = -k_{\text{OCl}}[\text{CNCl}][\text{OCl}^-]$ . At 25 °C, pH 7, and a free chlorine residual of 0.5 mg/L as  $\text{Cl}_2$ , the half-life of CNCl is approximately 60 min, suggesting significant decomposition is expected over disinfection time scales. Under some winter season temperature conditions, however, the decay half-life of CNCl can be longer than typical disinfection contact times. The results of this study demonstrate that the observed association of CNCl with chloramination systems can in part be explained by the differences in its stability with chlorine and chloramines.

## Introduction

Cyanogen chloride (CNCl, CAS 506-77-4) is a disinfection byproduct (DBP) found in chlorinated and chloraminated drinking water as well as wastewater (1–3). It is thought to form by the reaction of these disinfectants with natural organic matter. Model solution experiments, for example, have shown that CNCl is produced after the chlorination and chloramination of amino acids (4–10) and upon the chloramination of formaldehyde (11).

CNCl is acutely toxic and has long been used as a chemical warfare agent (12) and so its recently recognized presence in drinking water is of concern. Although the health risks due to chronic exposure to CNCl are not yet well defined, it has been listed on the USEPA Drinking Water Priority List (13), and many utilities were required to monitor CNCl concentrations in their water supplies under the Information Collection Rule (ICR) (14).

Progress in understanding the formation, fate, and health impact of CNCl requires first an understanding of its stability

under disinfection conditions. CNCl is known to hydrolyze slowly in water, and its hydrolysis can be assisted by hydroxide ( $\text{OH}^-$ ) (15)



and



where  $k_{\text{H}_2\text{O}}$  is the first-order rate constant of water hydrolysis and  $k_{\text{OH}}$  is the second-order rate constant of hydroxide-assisted hydrolysis. Reported values of  $k_{\text{H}_2\text{O}}$  are in close agreement, in which  $k_{\text{H}_2\text{O}} = 9.8 \times 10^8 e^{-10471/T}$ , where  $T$  is the absolute temperature in K and  $k_{\text{H}_2\text{O}}$  is given in  $\text{s}^{-1}$  (16–18). By reaction 1, CNCl has a half-life ( $t_{1/2}$ ) of hundreds of hours. There is somewhat greater uncertainty among literature values of  $k_{\text{OH}}$ ; however, these studies suggest that  $k_{\text{OH}}$  is less than  $10 \text{ M}^{-1} \text{ s}^{-1}$  over the temperature range of 5 to 25 °C (15, 17, 19–21). Under conditions relevant to water treatment, e.g.,  $\text{pH} < 8$ , the half-life of CNCl due to  $\text{OH}^-$ -assisted hydrolysis is still greater than 19 h. Based on reactions 1 and 2 alone, therefore, CNCl would be relatively stable in water at drinking water pH conditions.

Free chlorine is known to accelerate the decomposition of CNCl (17, 19–24) although the underlying mechanism is still unclear. It has been proposed that the accelerated decomposition of CNCl is due to either direct chlorination (17, 21) or a catalyzed hydrolysis (19, 20). In these earlier studies, different reactive free chlorine species were proposed to account for the accelerated effect. Proposed reactive species include dissolved molecular chlorine ( $\text{Cl}_{2,\text{aq}}$ ) (19) and hypochlorite ( $\text{OCl}^-$ ) (17, 21, 23). The resulting rate laws, summarized in Table 1, illustrate the range of decomposition models that exist in the literature. Using these rate laws to predict the effect of free chlorine, one might conclude that CNCl decomposition under common drinking water conditions could be slower (21), comparable to (20), or faster than (23) the rate due to hydroxide-assisted hydrolysis.

Cyanogen chloride can also be produced in systems using monochloramine ( $\text{NH}_2\text{Cl}$ ) as a primary disinfectant. Unfortunately, no comparable stability studies of CNCl in the presence of monochloramine are available. Occurrence data suggest an association of CNCl in treated drinking water with chloramine use (1). It was, in fact, such phenomenological based observations that led to a specific monitoring requirement within the ICR program, that only utilities employing chloramination included CNCl in their monitoring programs. Model kinetic studies have also suggested that potential formation pathways for CNCl exist during chloramine disinfection (11, 25). It is not clear, however, whether the apparent association of CNCl with chloramine use is due to greater rates of CNCl formation or a greater stability of CNCl in the presence of chloramines vs free chlorine.

In view of the uncertainty regarding the stability of CNCl under water disinfection conditions, the objective of this study was to examine the stability of CNCl in the presence of free chlorine and monochloramine, clarify the reaction mechanism, and use the kinetic data to assess the fate of CNCl once produced in a treatment facility. Membrane introduction mass spectrometry (MIMS) was employed to monitor aqueous concentrations of CNCl in real time.

## Materials and Methods

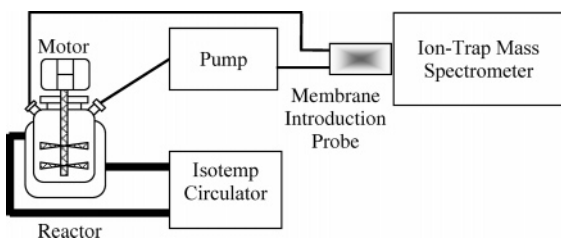
**Reagents.** All chemicals used in this study were of ACS Reagent Grade and most were obtained from Fisher Scientific,

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**TABLE 1. Kinetic Data for CNCl Decomposition with Free Chlorine from the Literature**

temp (°C)	rate law <sup>a</sup>	rate constant	ref
0	$\frac{d[\text{CNCl}]}{dt} = -k_{\text{OH},\text{Cl}}[\text{CNCl}][\text{OH}^-][\text{Cl}_2]_{\text{T}}$	$1.3 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$	(20)
10		$1.6 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$	
20		$1.7 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$	
20	$\frac{d[\text{CNCl}]}{dt} = \frac{d[\text{Cl}_2]_{\text{T}}}{dt} = -k_{\text{Cl}}[\text{CNCl}][\text{Cl}_2]_{\text{T}}$	$0.27(\pm 0.05) \text{ M}^{-1} \text{ s}^{-1}$	(21)
20	$\frac{d[\text{CNCl}]}{dt} = -k_{\text{OCI}}[\text{CNCl}][\text{OCI}^-]$	$40 \text{ M}^{-1} \text{ s}^{-1}$	(23)

<sup>a</sup>  $[\text{Cl}_2]_{\text{T}}$  = total free chlorine concentration.


**FIGURE 1. Temperature-controlled, continuously stirred batch reactor with in-line Membrane Introduction Mass Spectrometer (MIMS) monitoring system.**

except sodium phosphate salts, which were acquired from Sigma-Aldrich. Working stock solutions of hypochlorite were prepared by diluting 6% commercial NaOCl solution in deionized (DI) water and standardized daily before use. CNCl standards were prepared as needed from the 1:1 stoichiometric reaction of potassium cyanide (KCN) and sodium hypochlorite (NaOCl) in DI water according to a method used by Wu et al. (26). The same rapid stoichiometric reaction of KCN and NaOCl was used to generate solutions of CNCl as a reaction reagent in all kinetic experiments. Monochloramine was made from the 1:1 stoichiometric reaction of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and NaOCl (27). Monochloramine prepared at neutral pH was determined to have a purity of approximately 95% and to be stable for at least an hour by standard *N,N*-diethyl-*p*-phenylenediamine (DPD) titration (28). The solution pH was buffered over the range of 5.4–7.8 with 10 mM total phosphate prepared from mixtures of sodium salts. In one previously published study, phosphate was reported to accelerate the decomposition of CNCl (21). At the lower phosphate concentration of our experiments, however, their data would suggest less than a 2% decrease in CNCl should occur over a 60-minute period at pH 7.5. In the presence of phosphate buffer alone, our experiments confirmed that the concentration of CNCl does not detectably change over 30 min. Other investigators have similarly utilized phosphate buffers in the presence of CNCl without interference (19, 23). Chloride, which is present as an impurity in the commercial NaOCl reagent and as a product of the CNCl chlorination reaction, was also examined with respect to its effect on CNCl stability. No detectable decay of CNCl was observed when an equal concentration of NaCl was added, and hence the background chloride did not affect the reaction. Solutions of cyanide, cyanate, carbonate, bicarbonate, iodide, and other anions were made from the dissolution of either their sodium or potassium salts.

**In-Line Membrane Introduction Mass Spectrometry (MIMS).** Concentrations of CNCl in aqueous solution were measured directly and in real time by in-line membrane introduction mass spectrometry (MIMS) (29–32). By using MIMS, unlike other analytical methods (22, 33, 34), it was not necessary to quench the reaction. The apparatus shown in Figure 1 consists of a constant temperature and well-mixed batch reactor, an HPLC piston pump (Acuflow Series

I, Lab Alliance Inc.), a direct membrane inlet probe (MIMS Technology), and a Saturn 4D ion-trap mass spectrometer (MS) (Varian). The solution in the reactor was pumped to the membrane probe through PEEK tubing (0.50 mm i.d.) and after passing through the membrane, the solution was directed back to the reactor to eliminate headspace. The total volume outside the reactor was approximately 1.5 mL or about 1% of the reactor volume. To eliminate headspace, the sample loop was initially filled with DI water. The error introduced in such a manner was also about 1% and justifiably neglected. The pumping rate was 2 mL/min, and, therefore, less than half a minute was required for the solution to travel from the reactor to the membrane. Since the sample loop tubing was well-insulated, temperature changes in the tubing were negligible over the half minute fluid residence time.

The pump was started at time zero when the reactants were mixed, so the initial contact of reaction solution with the membrane occurred at approximately 0.5 min. In addition to the residence time delay, there was a lag time for the analyte to achieve steady state at the membrane due to mass transfer limitations. In total, the response time of the MIMS system was approximately 3 min, and only data collected after 5 min were used in kinetic analysis as a safety factor.

Permeation of CNCl occurs through the silicone membrane tubing (0.64 mm i.d. – 1.19 mm o.d.  $\times$  ~2 cm length, Fisher Scientific) that separates the aqueous phase from the MS inlet. The MS operated in the electron impact (EI) mode and the spectrum of CNCl showed characteristic peaks at mass-to-charge ( $m/z$ ) values of 62 and 64. The MS was automatically tuned by the instrument using the generic calibrant FC 43 (perfluorotributylamine). Quantitative measurements of CNCl were achieved based on the linear relation between the sum of ion counts at  $m/z$  values of 62 and 64 of CNCl mass transfer through the membrane (MS signal) and its aqueous concentration. Such a linear relationship was observed up to 30  $\mu\text{M}$  of CNCl in water with a detection limit ( $S/N = 3$ ) estimated to be 0.09  $\mu\text{M}$ . Loss of CNCl passing through the membrane had no measurable effect on the reaction solution composition. It was observed that the concentration of CNCl in water at neutral or acidic pH was unchanged for 30 min while flowing through the MIMS system. Hence, the analysis of CNCl concentration by the MIMS system was virtually nondestructive. Besides CNCl, other reaction products were also detectable directly using the MIMS.

**Other Analytical Methods.** The CNCl solution used to calibrate the MIMS was standardized by a standard colorimetric method (28) using a Hitachi model 2000 spectrophotometer. Free chlorine stock solutions were standardized in terms of their UV absorbance at 292 nm ( $\epsilon_{\text{OCl},\text{max}} = 350 \text{ M}^{-1} \text{ cm}^{-1}$ , 25 °C and pH > 9.5) (35–37) or by standard DPD titration (28). The decay kinetics of free chlorine in the presence of CNCl was measured by the standard DPD colorimetric method (28). After taking a sample, free chlorine measurements were complete within 10 s. The presence of CNCl did not affect the development of color with DPD.

Cyanate was measured by ion-exchange chromatography (IC) (Dionex 100) with a conductivity detector and an eluent consisting of 3.1 mM Na<sub>2</sub>CO<sub>3</sub> and 1.0 mM NaHCO<sub>3</sub>. Prior to the cyanate analysis, the reaction of CNCl and free chlorine was immediately quenched with a 2-fold excess of cyanide, and the formed CNCl was then removed from the sample by degassing with helium (He) in order to prevent its decomposition in the IC eluent (pH = 10.4) during the analysis. In a previous study, cyanide was reported to accelerate the decomposition of CNCl but at higher cyanide concentrations (19). At the cyanide concentrations used in our experiments, approximately 60 μM, their data suggest less than a 2% decrease in CNCl should occur over 60 min. In the presence of 60 μM cyanide alone at pH 7, our experiments confirmed that the concentration of CNCl did not detectably change over 30 min, which is conservatively longer than the CNCl degassing period.

Solution pH was measured with a combined micro glass electrode (Accumet) that was calibrated with standard buffer solutions (Fisher Scientific).

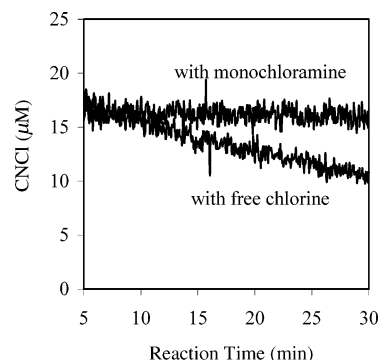
**Experimental Procedures.** The stability of CNCl in the presence of free chlorine and monochloramine was initially compared at pH 7 at 25 °C with approximately 14 μM (1.1 mg/L as Cl<sub>2</sub>) free chlorine or monochloramine and approximately equimolar concentrations of CNCl. Subsequent kinetic studies of the reaction of CNCl with free chlorine were conducted with less than 3 μM CNCl and at least 10-fold excess of chlorine in buffered solution. CNCl was instantaneously formed by the reaction of cyanide and chlorine stoichiometrically. The initial free chlorine dose, buffer pH, and reaction temperature were varied in order to study the reaction dependence on total free chlorine, pH, and temperature and obtain estimates of rate constants. The experiments were conducted over the pH range of 5.4 to 7.8. At pH < 8, the hydroxide-assisted hydrolysis of CNCl is negligible. Four different constant temperature conditions were examined over the range 5 to 35 °C to model the temperature dependence of the reaction rate.

The reaction mechanism of CNCl and free chlorine was further investigated in a separate experiment with nearly equimolar initial concentrations (24 μM) of each reactant by monitoring the change in free chlorine, CNCl, and the formation of two products—cyanate and trichloramine, at pH 7. In this experiment, CNCl and trichloramine were monitored on-line by MIMS, free chlorine was assayed in 0.5 mL aliquots removed by pipet from the 100 mL reactor. Cyanate was measured after quenching 100 mL reaction solution with cyanide and purging the remaining CNCl.

## Results and Discussion

**Relative Stability of CNCl with Disinfectants.** Cyanogen chloride was significantly less stable in the presence of free chlorine relative to monochloramine. As shown in Figure 2, with approximately 14 μM (1.1 mg/L as Cl<sub>2</sub>) free chlorine and a nearly equal molar concentration of CNCl (approximately 17 μM CNCl), the concentration of CNCl was reduced to approximately 10 μM in 30 min at pH 7 and 25 °C. Under the same conditions, the concentration of CNCl remained virtually unchanged over 30 min when monochloramine was present. As described above, CNCl concentrations are only reported after the 5 min response time of the MIMS.

The greater stability of CNCl with monochloramine relative to free chlorine is likely to explain in part the association of CNCl with chloramine disinfection systems (1, 2). To estimate how important the decay rate of CNCl is in free chlorine systems and explain the difference in reactivity between free chlorine and monochloramine, it was first necessary to refine our understanding of the mechanism and the rate law.



**FIGURE 2.** CNCl decomposition with free chlorine or monochloramine. Experiments were conducted with approximately 14 μM (1 mg/L as Cl<sub>2</sub>) disinfectant and 17 μM initial CNCl at pH 7.

### Dependence of CNCl Decay on Its Own Concentration.

To obtain the rate law, the dependence of CNCl decay on its own concentration was determined with chlorine in excess. The reaction was examined with approximately 2.0 μM CNCl and 30 μM (2.1 mg/L as Cl<sub>2</sub>) of free chlorine at pH 6.9 and 25 °C. Measurements of the free chlorine concentration showed that it varied by less than 10% after 30 min. As shown in Figure 3, except during the initial period of mass transfer, the concentration of CNCl follows a pseudo-first-order decay with respect to its own concentration:

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

The pseudo-first-order rate constant,  $k_{\text{obs}}$ , was obtained from the integrated form of eq 3, written as

$$\ln[\text{CNCl}] = \ln[\text{CNCl}]_0 - k_{\text{obs}}t \quad (4)$$

where  $[\text{CNCl}]_0$  is the concentration at  $t = 0$ . The regression was conducted using the experimental data from 5 to 30 min as shown in Figure 3.

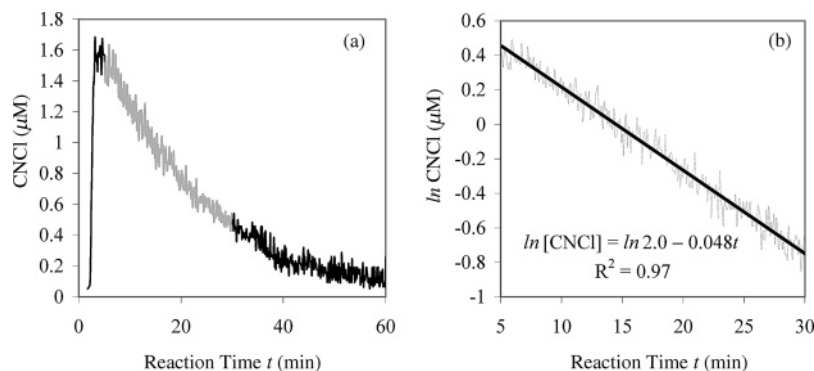
**Dependence of CNCl Decay on the Concentration of Free Chlorine.** Using the analysis illustrated in Figure 3,  $k_{\text{obs}}$  was estimated at varying concentrations of excess free chlorine ( $[\text{Cl}_2]_{\text{T}} = 16\text{--}48 \mu\text{M}$ ) at an average pH 6.83 ( $\pm 0.03$ ) and 25 °C. A plot of  $k_{\text{obs}}$  as a function of the total free chlorine concentration reveals a linear relationship, as shown in Figure 4

$$k_{\text{obs}} = k_{\text{Cl}}[\text{Cl}_2]_{\text{T}} \quad (5)$$

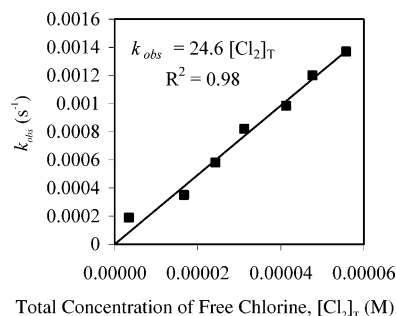
where  $k_{\text{Cl}}$  is the slope of the linear regression and  $[\text{Cl}_2]_{\text{T}}$  is the total concentration of free chlorine, i.e.,  $[\text{OCl}^-] + [\text{HOCl}]$ . The value of  $k_{\text{Cl}}$  was determined as 24.6 M<sup>-1</sup> s<sup>-1</sup> under these experimental conditions. CNCl decay rates, therefore, have a pseudo-first-order dependence on the concentration of free chlorine. Combining eqs 3 and 5, the apparent rate law can be expressed as

$$\frac{d[\text{CNCl}]}{dt} = -k_{\text{Cl}}[\text{Cl}_2]_{\text{T}}[\text{CNCl}] \quad (6)$$

**pH Dependence.** To investigate the reactive species of free chlorine that accounts for the accelerated decay of CNCl, the pH dependence of the reaction was studied over the pH range of 5.4 to 7.8 at 25 °C. The total free chlorine concentrations were again in excess at approximately 30 μM (actual range was 28.4–30.6 μM) and the initial CNCl concentrations less than 3 μM. The pseudo-second-order rate constant in eq 5,  $k_{\text{Cl}}$ , increased from 0.9 to 73 M<sup>-1</sup> s<sup>-1</sup> as shown in Figure 5(a).

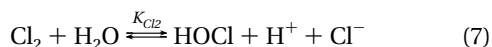


**FIGURE 3.** (a) Example CNCl decay in the presence of free chlorine as monitored by MIMS. Solution contained approximately 2.0  $\mu\text{M}$  CNCl and 30  $\mu\text{M}$  (2.1 mg/L as  $\text{Cl}_2$ ) free chlorine at 25  $^\circ\text{C}$  and pH 6.9. (b) Pseudo-first-order dependence of CNCl decay on its own concentration between 5 and 30 min shown as gray line. Dark line in (b) describes a linear least-squares regression of gray portion of data in (a) to eq 4.



**FIGURE 4.** Pseudo-first-order dependence of CNCl decay on the concentration of free chlorine. Experiments were conducted with free chlorine in excess at 25  $^\circ\text{C}$  and an average pH 6.83 ( $\pm 0.03$ ). The slope of the linear regression (solid line) is  $k_{Cl}$ .

Molecular aqueous chlorine,  $\text{Cl}_{2,\text{aq}}$ , was proposed in one earlier study as the reactive chlorine species (19). Based on the equilibrium,



where  $K_{Cl_2} = 10^{3.5} \text{ M}^2$  is the equilibrium constant at 25  $^\circ\text{C}$  (38), the concentration of the unhydrated form of chlorine should decrease with increasing pH, and hence the interpretation of  $\text{Cl}_2$  as the reactive species is inconsistent with the observed pH dependence of the reaction. Furthermore, since there is at most  $10^{-4} \text{ M}$  chloride ion present (i.e., as an impurity in the stock NaOCl solution), the fraction  $([\text{Cl}_2]/[\text{Cl}_2]_T)$  should be less than  $10^{-14.6}$  at pH 7. If the rate determining step involved  $\text{Cl}_2$ , the reaction would have to be much faster than a diffusion-controlled reaction, based on the estimate for  $k_{Cl}$  in Figure 4.

Previous proposals, that hypochlorite ion is the reactive chlorine species, are, on the other hand, more plausible (17, 21, 23). Since the  $pK_a$  for hypochlorous acid is 7.55 at 25  $^\circ\text{C}$  (37), the fraction of chlorine present as  $\text{OCl}^-$  would increase significantly as pH increases over the range studied here. We considered the participation of both acid and conjugate base forms and found that the pH dependence of the reaction can be modeled in terms of hypochlorite alone, i.e.,

$$\frac{d[\text{CNCl}]}{dt} = -k_{\text{OCl}}\alpha[\text{Cl}_2]_T[\text{CNCl}] \quad (8)$$

where the fraction of chlorine present as  $\text{OCl}^-$  is  $\alpha = K_a/(K_a + [\text{H}^+])$ , and  $k_{\text{OCl}}$  is a second-order rate constant. Since  $k_{Cl} = k_{\text{OCl}}\alpha$ , the model given by eq 8 can be tested by plotting values of  $k_{Cl}$  obtained at various pH conditions vs  $\alpha$ , as shown

in Figure 5(b). The slope of the linear least-square regression is the second-order rate constant,  $k_{\text{OCl}}$ . At 25  $^\circ\text{C}$ ,  $k_{\text{OCl}} = 121(\pm 2) \text{ M}^{-1} \text{ s}^{-1}$ , and the rate law can be written as

$$\frac{d[\text{CNCl}]}{dt} = -k_{\text{OCl}}[\text{OCl}^-][\text{CNCl}] \quad (9)$$

Based on our experimental and modeling results, the reactive chlorine species is hypochlorite ion as proposed (17, 21, 23).

#### Decay Products of CNCl in the Presence of Free Chlorine.

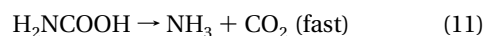
Under alkaline conditions in industrial cyanide treatment by chlorination, cyanate is a known product (39); the reaction is thought to proceed through CNCl as an intermediate. At the neutral pH conditions of our experiments, and with equimolar concentrations of CNCl and free chlorine, cyanate was also found to be the primary decay product of CNCl. As shown in Figure 6(a), the sum of the concentrations of CNCl and  $\text{CNO}^-$  satisfies a mole balance for carbon and nitrogen during a reaction period of 30 min.

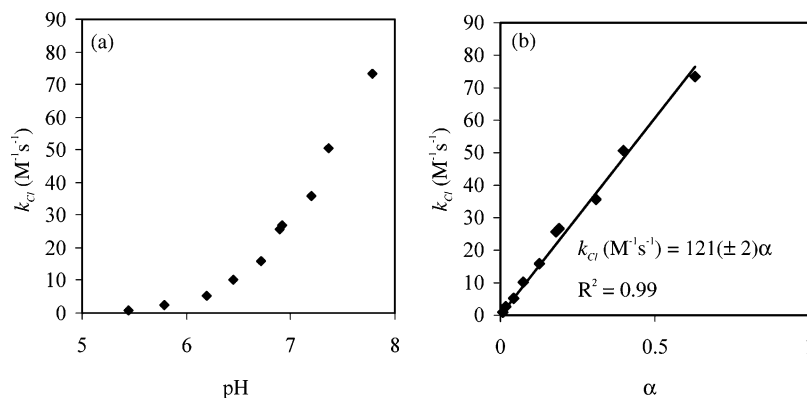
Spectral evidence of other decay products in these experiments, chloramines, was also obtained from the MIMS as well, as shown in Figure 6(b),(c). Characteristic abundances of 3:1 at  $m/z$  49 and 51, 10:6:1 at  $m/z$  84, 86, and 88, and 3:3:1 at  $m/z$  119, 121, and 123 suggest the production of  $\text{NCl}^+$ ,  $\text{NCl}_2^+$ , and  $\text{NCl}_3^+$ , respectively. The spectrum is consistent with the mass spectrum reported for trichloramine (31). An upper limit concentration estimate for trichloramine was calculated as 2  $\mu\text{M}$  based on its ion abundance ( $m/z$  84) at 30 min. Trichloramine, although detectable, was apparently not a significant species in the N mole balance, given that the summation of CNCl and  $\text{CNO}^-$  nitrogen was 24  $\mu\text{M}$  with a 95% confidence interval of approximately 2  $\mu\text{M}$ , and the total initial CNCl-nitrogen concentration was also 24  $\mu\text{M}$ .

Previous investigations of cyanate decomposition by free chlorine have been conducted at relatively alkaline solution conditions (16, 20, 40–42). At pH > 8.7, cyanate decomposition rates were first order with respect to total cyanate, total free chlorine, and  $\text{H}^+$ , and the reaction was proposed to involve the hypochlorite-catalyzed hydrolysis of cyanic acid (43, 44). Cyanic acid hydrolysis in the absence of chlorine is thought to proceed by the initial formation of carbamate, ( $\text{H}_2\text{NCOOH}$ ) which rapidly decomposes to give ammonia and carbonate (42)

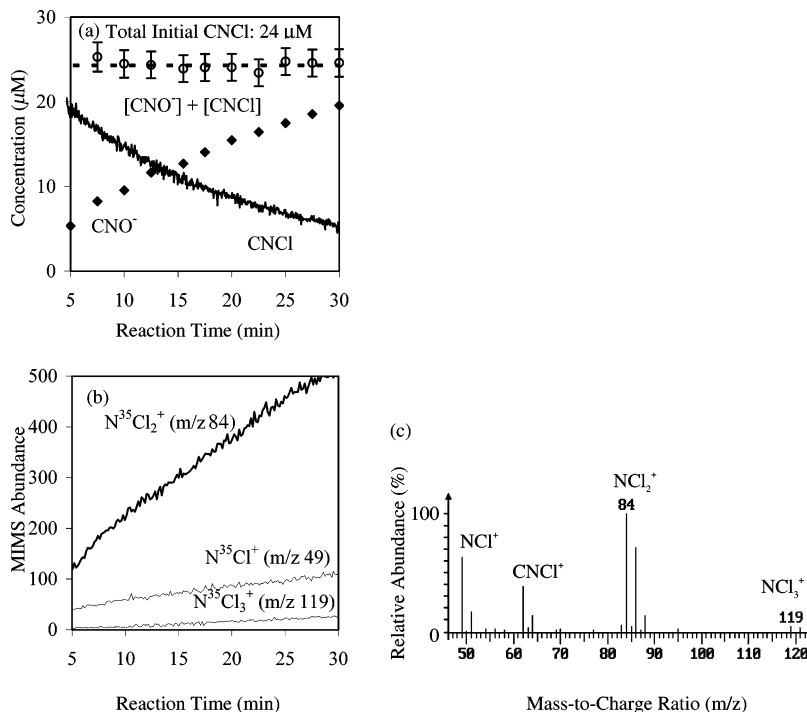


and





**FIGURE 5.** Dependence of  $k_{Cl}$  on pH. The abscissa of (b) is the fraction of free chlorine as  $OCl^-$  and the slope is  $k_{OCl}$  in  $M^{-1} s^{-1}$ . Experiments were conducted at 25 °C.

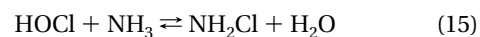
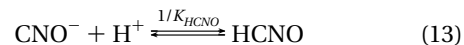


**FIGURE 6.** Decay products of CNCl in the presence of free chlorine. Experiments conducted with approximately 24  $\mu M$  CNCl and equal molar ratio of free chlorine at pH 7 and 25 °C. (a) Decay of CNCl and formation of cyanate with time. The solid line represents the concentration of CNCl. The dashed line represents the initial CNCl concentration of 24  $\mu M$ . Diamonds represent cyanate concentration. Open circles represent the sum of CNCl and cyanate, i.e.,  $[CNCl] + [CNO^-]$ . The 95% confidence intervals of the estimates of  $[CNCl] + [CNO^-]$  are shown by the error bars. (b) Formation of chloramine with time; and (c) MIMS spectrum at 15 min.

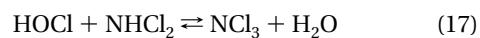
In the presence of free chlorine, ammonia would rapidly react to form chloramines, and thus the detection of trichloramine is consistent with a cyanic acid hydrolysis pathway.

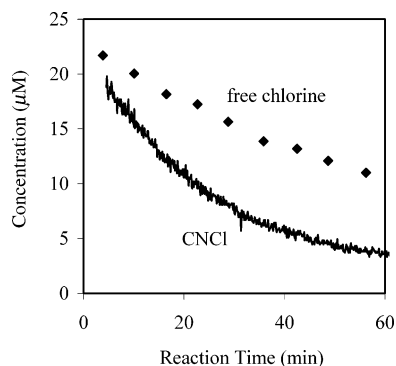
**Role of Hypochlorite.** To further examine the role of hypochlorite in accelerating CNCl decomposition, the disappearance of free chlorine and CNCl were monitored simultaneously in solutions containing nearly equimolar concentrations of both reagents. The experimental results, shown in Figure 7, indicate that while free chlorine concentrations do decrease, the decrease was much slower than the decay of CNCl. Over 60 min, more than 75% of CNCl decomposed, while less than 50% of the chlorine disappeared. These kinetic profiles suggest that hypochlorite acted as a catalyst, and given that cyanate was the primary product, it appears that  $OCl^-$  served to catalyze the hydrolysis of CNCl. The later consumption of free chlorine could in part be a result of its subsequent rapid reaction with small amounts of ammonia to form trichloramine.

A reaction scheme consistent with the observed products and the catalytic role of hypochlorite is as follows:

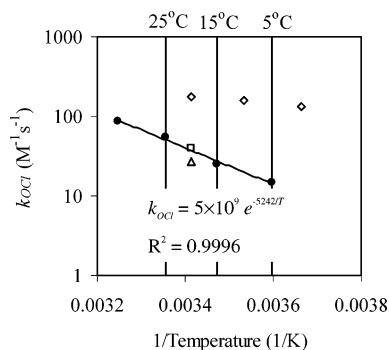


and



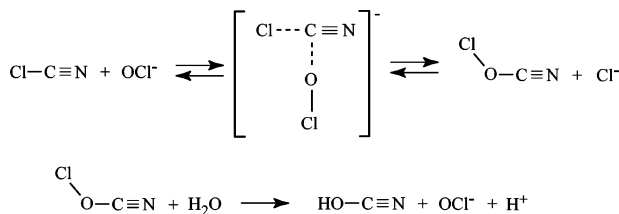


**FIGURE 7. Decay rate comparison of CNCl and free chlorine. Experiments conducted with approximately 24 µM CNCl and equal molar ratio of free chlorine at pH 7 and 25 °C.**



**FIGURE 8. Values of  $k_{OCl}$  at various temperatures.  $\diamond$  Eden and Wheatland (1950) (recalculated),  $\square$  Xie and Reckhow (1993),  $\triangle$  Price et al. (1947) (recalculated),  $\bullet$  is the absolute temperature. Solid line is a linear regression of data obtained in this study.**

**SCHEME 1**



The catalytic effect of hypochlorite ion could be explained by either a nucleophilic attack pathway or a general base-catalyzed mechanism. The former mechanism would imply a rate dependence on the nucleophilic reactivity of the catalyst toward the carbon, whereas the rate would depend on the base strength of the catalyst if a general base-catalyzed path was operative. As Edwards et al. (17) have

pointed out, the reactivity of hypochlorite and CNCl is poorly predicted by a Bronsted-type correlation of base strength, and thus a nucleophilic attack mechanism is more plausible. Catalysis by this path would involve first the rate-limiting release of the leaving group  $\text{Cl}^-$ , and the formation of an unstable intermediate that is rapidly hydrolyzed, as shown in Scheme 1.

Additional evidence supporting Scheme 1 as the catalytic pathway is the observation by Bailey and Bishop (19) that chloride at a concentration of at least 20 mM can inhibit the decomposition of CNCl.

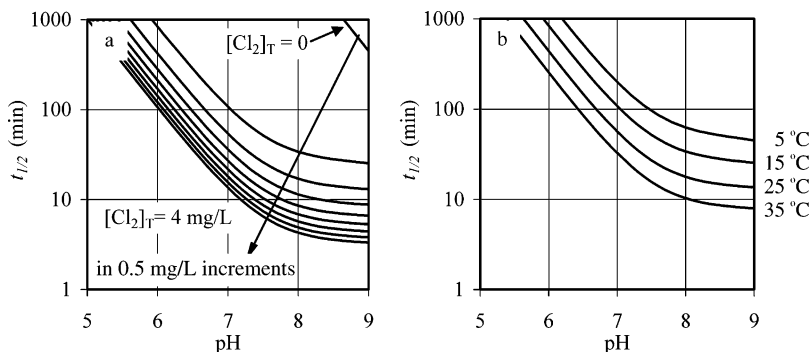
**Temperature Dependence of CNCl Decomposition.** The reaction rate constant,  $k_{OCl}$ , for reaction 12 and eq 9 was estimated as a function of temperature over the range of 5 to 35 °C. The temperature dependence of the acidity constant for HOCl reported in the literature (37) was assumed in these calculations. An Arrhenius fit of the temperature dependence is plotted in Figure 8 and compared with previous reported and recalculated values of  $k_{OCl}$  from the literature. The values of  $k_{OCl}$  determined in this study fall in the middle of the range reported in previous studies but show a greater sensitivity to temperature change. This temperature dependence, given in the form of the Arrhenius equation, is

$$k_{OCl} (\text{M}^{-1} \text{s}^{-1}) = 5 \times 10^9 e^{-5242/T} \quad (18)$$

where  $T$  is absolute temperature in K, and the activation energy is 43 kJ/mol.

**Implications for Drinking Water Disinfection.** In model solutions, common organic compounds, such as amino acids, are known to react with free chlorine to form CNCl (4, 8, 10). In water quality surveys of drinking water treatment plant effluents, however, CNCl is also found in plants utilizing free chlorine, but in generally smaller concentrations than facilities using chloramines (1). Cyanogen chloride hydrolysis can be an important reaction mitigating the CNCl yield observed in disinfection processes but only in chlorination systems due to the catalytic effect of hypochlorite. By contrast, when chloramine is used as disinfectant, CNCl is much more stable.

The importance of the hypochlorite-catalyzed hydrolysis pathway in mitigating CNCl yields can be illustrated by using the models determined in this study to predict the half-life of CNCl under drinking water conditions. The half-life of CNCl in a hypothetical chlorination system is modeled in Figure 9 as a function of chlorine residual concentration, pH, and temperature. As shown in Figure 9, the half-life is 56 min at pH 7 and 25 °C with 0.5 mg/L  $\text{Cl}_2$ . At 15 °C, however, the half-life increases to 107 min, all other solution conditions remaining the same. Contact times for chlorine disinfection inside treatment facilities are commonly in the range of 10–60 min. Based on these estimates, extensive CNCl hydrolysis is expected over the time scale of the process,



**FIGURE 9. Simulation of CNCl stability in terms of its half-life for conditions relevant to drinking water disinfection. Left figure was estimated at 15 °C at various free chlorine concentrations. Right figure was obtained with 0.5 mg/L as  $\text{Cl}_2$  at various temperatures. Free chlorine is assumed in large excess in both simulations.**

although at colder temperatures, CNCl hydrolysis is much less likely to be complete.

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