Chlorination of Urea I: Reaction Mechanism -
Supporting Information

Ernest R. Blatchley III, Ph.D, P.E., BCEE
Professor, School of Civil Engineering and Division of Environmental & Ecological Engineering
Purdue University, West Lafayette, IN 47907-2051, USA
blatch@purdue.edu

and

Mingming Cheng, Ph.D.
Post-Doctoral Research Associate, School of Civil Engineering
Purdue University, West Lafayette, IN 47907-2051, USA
cheng@purdue.edu
Table SI-1. Ranges of measured concentrations of urea in pool water samples. Pool names are excluded from this list at the request of pool owners.

<table>
<thead>
<tr>
<th>Facility/Pool</th>
<th>Urea Concentration (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Natatorium Competition Pool</td>
<td>0.17</td>
</tr>
<tr>
<td>Natatorium Diving Well</td>
<td>0.17</td>
</tr>
<tr>
<td>Natatorium Spa</td>
<td>0.20</td>
</tr>
<tr>
<td>High School A</td>
<td>0.82</td>
</tr>
<tr>
<td>High School B</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Figure SI-1. Inorganic chloramine concentration (measured by MIMS) as a function of Cl:P ratio for a fixed reaction time (t = 5 hr), pH = 6.5, and T = 25°C. Initial urea concentration = 5.0 x 10^{-5} M. Spline fits (dashed lines) are included to illustrate trends in the data.
Spectrophotometric measurements were used to examine the behavior of urea, N-chlorourea, and chlorine in aqueous solution. Aqueous solutions of pure compounds were prepared for use in these measurements.

Figure SI-2 illustrates molar absorptivity as a function of wavelength for aqueous solutions of urea. Reported values of molar absorptivity were based on absorbance measurements that ranged between $0.010 \leq A \leq 1.00$.

![Figure SI-2. Molar absorptivity of urea. Values reported in this figure are based on absorbance measurements that ranged between 0.010 and 1.00.](image)
Figure SI-3 illustrates the molar absorptivity of N-chlorourea. The concentration of N-chlorourea present in solution was measured by the DPD/KI spectrophotometric method and this measurement confirmed complete transfer of +1-valent chlorine to the urea molecule. This experiment was conducted under conditions of low Cl:P molar ratio. The concentration of N-chlorourea measured by the DPD/KI spectrophotometric method was consistent with the loss of free chlorine in the system. The resulting concentrations of urea and N-chlorourea were calculated by mass balance, and the N-chlorourea absorbance spectrum was calculated from the measured absorbance spectrum of the mixture and the concentrations of urea and N-chlorourea.

![Absorbance Spectrum](attachment:image)

**Figure SI-3.** Molar absorptivity for N-chlorourea in aqueous solution.

\[ \varepsilon_{245} = 245 \text{ M}^{-1}\text{cm}^{-1} \]
Figure SI-4. N-chlorourea yield after four hours of exposure to free chlorine at pH = 5.0 for a range of chloride ion concentrations. Note that the chloride ion concentration is illustrated in a log$_{10}$ scale. The horizontal blue line indicates the free chlorine concentration added at $t = 0$. The red line indicates the fraction of free chlorine that was present in the form of molecular chlorine ($\alpha_{\text{Cl}_2}$).
Figure SI-5. Measurements of [N-Chlorourea] as a function of time for the first 0.10 s of a reaction between free chlorine and urea, based on $A_{245}$ measurements in a stopped-flow device. Initial conditions of the experiment were: urea concentration $= 4.0 \times 10^{-4}$ M, free chlorine concentration $= 1.0 \times 10^{-4}$ M; pH $= 2.0$; and chloride concentration $= 0.01$ M.
In multi-component mixtures, spectrophotometric measurements need to account for absorbance by other components of the reacting system. In particular, it is relevant to consider absorbance by the components of free chlorine. Absorbance spectra for free chlorine solutions ([free chlorine] = 1.41 x 10^{-4} M; [Cl\textsuperscript{-}] = 9.75 x 10^{-3} M) were measured at pH = 1.80, pH = 4.35, and pH = 10.26 (see Figure SI-6). The data presented in Figure SI-6 were used to develop estimates of molar absorptivity for each of the components of free chlorine: Cl\textsubscript{2}, HOCl, and OCl\textsuperscript{-}. This was accomplished by application of Beer’s law for multi-component mixtures. For this application, it was assumed that absorbance at each wavelength was attributable to only the free chlorine components. Mathematically, this allowed for expression of absorbance as follows:

\[
\left(\frac{A_\lambda}{\varepsilon}\right)_{\mu m} = \varepsilon_{Cl_2} \cdot C_{Cl_2} + \varepsilon_{HOCl} \cdot C_{HOCl} + \varepsilon_{OCl^-} \cdot C_{OCl^-}
\]

where,
- \(A_\lambda\) = solution absorbance at wavelength = \(\lambda\)
- \(\varepsilon\) = optical path length for absorbance measurement (cm)
- \(\varepsilon_{i\lambda}\) = molar absorptivity of \(i^{th}\) constituent in solution at wavelength = \(\lambda\) (M\(^{-1}\)⋅cm\(^{-1}\))
- \(C_{i}\) = concentration of \(i^{th}\) constituent in solution (M).

For the solutions that were used for the measurements listed in Figure SI-6, it was possible to determine the molar concentrations of all constituents by knowledge of the total free chlorine concentration, and the ionization fractions for the free chlorine constituents. Therefore, in equation (1), the unknowns were the values of molar absorptivity for the three constituents of interest: \(\varepsilon_{Cl_2}\), \(\varepsilon_{HOCl}\), and \(\varepsilon_{OCl^-}\). By repeating the absorbance scan at three different values of pH, it was possible to adjust the known concentrations of Cl\textsubscript{2}, HOCl, and OCl\textsuperscript{-}. Using linear algebra, it was then possible to develop estimates of the absorbance cross-sections for Cl\textsubscript{2}, HOCl, and OCl\textsuperscript{-} (see Figure SI-7). These data are consistent with published values of the absorbance cross-sections of HOCl and OCl\textsuperscript{-} for wavelengths greater than approximately 230 nm \((I)\). No published values for the molar absorptivity of Cl\textsubscript{2} were found to compare with the data presented in Figure SI-7.
Figure SI-6. Absorbance spectra of free chlorine solutions at several values of pH. Solution chemistry was defined by: [Free Chlorine] = 1.41 \times 10^{-3} \text{ M}; [\text{Cl}^-] = 9.75 \times 10^{-3} \text{ M}.
Figure SI-7. Molar absorptivity of Cl$_2$, HOCl, and OCl$^-$ at room temperature. At $\lambda=245$ nm, $\varepsilon_{\text{Cl}_2} = 56.1$ M$^{-1}$cm$^{-1}$; $\varepsilon_{\text{HOCl}} = 150$ M$^{-1}$cm$^{-1}$; and $\varepsilon_{\text{OCl}^-} = 51.0$ M$^{-1}$cm$^{-1}$. 
As further support for the hypothesis that the first N-chlorination reaction is a rate-limiting step in urea chlorination, consider the data presented in Figure SI-8. For this experiment, aqueous solutions of urea or N-chlorourea were chlorinated, and solution absorbance at 292 nm ($A_{292}$) was monitored as a function of time. $\lambda = 292$ nm represents a wavelength where hypochlorite ion (OCl$^-$) absorbs strongly (see Figure SI-7), but N-chlorourea and urea do not absorb strongly (see Figures SI-1 and SI-2). As such, measurements of $A_{292}$ allow for examination of the dynamics of free chlorine behavior based on an optical measurement.

*Figure SI-8.* Optical measurement of the dynamic behavior of free chlorine based on reactions with urea and N-chlorourea. Initial conditions: pH = 7.5; [urea] = [chlorourea] = [free chlorine] = $1.7 \times 10^{-4}$ M; therefore, Cl:P = 1:1.

The data in Figure SI-8 indicate that for the concentrations of urea and free chlorine present in solution, urea reacts with free chlorine at pH = 7.5 on a time scale of tens of hours, whereas N-chlorourea reacts to completely consume free chlorine within roughly one hour. Again, this supports the hypothesis that the first chlorination of urea represents a rate-limiting step in the overall mechanism of urea chlorination; moreover, the product of this first reaction (N-chlorourea) appears to react relatively rapidly with free chlorine to form other compounds.
REFERENCES