Chemistry of Nitrogen Compounds in Swimming Pool Water

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Nitrogen–containing impurities (e.g., ammonia, amino acids, creatinine, uric acid, etc.) introduced into swimming pools by bathers react with free available chlorine to form combined chlorine compounds. Because these compounds do not readily hydrolyze to hypochlorous acid, they are poor disinfectants. In effect, these combined chlorine compounds adversely affect disinfection by consuming free available chlorine. Ammonia is readily oxidized by free chlorine by the process of breakpoint chlorination. Amino acids are also decomposed by excess free chlorine although at a slower rate. Creatinine is similarly decomposed but the process is very slow. Ammonia derived chloramines are inherently unstable in the presence of sunlight because they absorb ultraviolet light. Indeed, monochloramine although stable in the absence of sunlight and free chlorine, is largely oxidized (~67%) to elemental nitrogen in the absence of free chlorine and the presence of sunlight. It is worth noting that it is urea and not ammonia that is the major nitrogen–containing bather contaminant in swimming pools and spas. Surprisingly, urea does not itself form combined chlorine and also does not appear to affect disinfection. However, urea has to be destroyed by oxidation because it is a nutrient for bacteria and algae and a source of ammonia chloramines. Oxidation of urea by free chlorine is a slow process that gives rise to transient ammonia chloramines (e.g., di– and trichloramine). Oxidation of other organic nitrogen compounds by chlorine also forms transient ammonia chloramines.

Bather Contaminants

Bathers introduce an average of 20–30 mL of urine into swimming pool water (Gunkel and Jessen 1988), the amount being greater for adults than for children. The distribution of nitrogen from the main nitrogen species in urine shown in Table 1 (White 1972), indicate that urea is the principle component of urine, amounting to approximately 20 g/L.

The urea introduced into swimming pools via urine ranges from 340 to 850 mg per bather; by contrast, sweat contributes an average of only 37 mg of urea per bather (Gunkel and Jessen 1988). The urea concentration in sweat is much lower than in urine (i.e., ~0.5 g/L). The other nitrogen–containing constituents of sweat are in general similar to those in urine with some variation in concentrations. Table 1 shows that ammonia, often thought to be the major source of chloramines, is only a minor constituent of urine.

Compound	% of Total Nitrogen
Urea	86.9
Ammonia	4.4
Amino Acids	4.3
Creatinine	3.6
Uric Acid	0.7

Table 1 – Distribution of Nitrogen Species in Urine

Compound	Taste and Odor ppm	Eye Irritation ppm
Free av. Cl (i.e., HOCl + ClO⁻)	20	20–30
Monochloramine	5	4
Dichloramine	0.8	
Trichloramine (Nitrogen trichloride)	0.02	
Urea + Av. Cl		10

Table 2 – Taste, Odor and Eye Irritation Threshold of Free and Combined Chlorine

Effect of Free and Combined Chlorine on Eye Irritation

Ammonia derived chloramines can cause taste and odor problems in water and may also cause eye irritation. Table 2 shows the taste and odor threshold of free and combined chlorine in the form of ammonia chloramines (White 1972). Data on eye irritation (Jandik 1977) shows that it also correlates with taste and odor data. Although ammonia chloramines are eye irritants at sufficiently high concentrations, the effect varies from insignificant for monochloramine to definite for trichloramine which is the main offender. The data show that free chlorine does not contribute to eye irritation at normal concentrations found in pools. Studies have shown that pH can also affect eye irritation (Mood et al 1951). Extended bather periods can also contribute to eye irritation.

Effect of Nitrogen Compounds on Combined Chlorine and Disinfection

The effects of the various nitrogen compounds on combined chlorine and on disinfection are summarized in Table 3. It is seen that urea, the major swimming pool/spa contaminant, is singularly conspicuous in that it does not form significant amounts of combined chlorine (Palin 1950) or affect disinfection (Fitzgerald and Der Vartanian 1967). Otherwise it would make swimming pool disinfection extremely difficult if not impossible. This indicates that urea does not form significant concentrations of chlorinated derivatives. However, urea has to be destroyed by oxidation because it is a nutrient for bacteria and algae and a source of ammonia chloramines. It is also seen that, by contrast with ammonia, the organic nitrogen compounds are oxidized slowly.

Decomposition of Ammonia Chloramines by Sunlight

Although monochloramine is relatively stable

Compound	Forms Combined Chlorine	Affects Disinfection	Rate Of Oxidation
Ammonia	Yes	Yes	Fast
Amino Acids	Yes	Yes	Slow
Urea	No	No	Very Slow
Creatinine	Yes	Yes	Very Slow
Uric Acid	Yes	Yes	Very Slow

Table 3 – Effect of Nitrogen Compounds on Combined Chlorine and Disinfection

Chloramine	Absorptivity L/mol/cm at 300 nm
Monochloramine	25
Dichloramine	293
Trichloramine	165

Table 4 – Absorptivity of Ammonia Chloramines

Compound	Av. Cl / N Mol Ratio	pH	CA ppm	% Decomposition
				10 min.
Ammonia	0.9	7.5	0	6
"	1.8	7.5	0	38
"	3.6	7.5	0	87
"	1.8	8.0	0	29
"	1.8	7.5	50	33
" + 40 ppm Br⁻	1.8	7.5	0	79
				60 min.
Urea	1.8	7.5	0	7[A]
"	1.8	8.0	0	7
"	3.6	7.5	0	8[B]
"	1.8	7.5	50	2
" + 40 ppm Br⁻	1.8	7.5	0	14[C]
Creatinine	1.8	7.5	0	8[D]
"	1.8	7.5	50	7
" + 40 ppm Br⁻	1.8	7.5	0	6
Glycine	1.8	7.5	0	60
"	1.8	7.5	50	52
" + 40 ppm Br⁻	1.8	7.5	0	>79
Alanine	1.8	7.5	0	66
Lysine	1.8	7.5	0	35

A) Decomposition after 24 and 48 hours was 21 and 34%, respectively.

B) Decomposition after 24 and 48 hours was 33 and 54%, respectively.

C) Decomposition after 24 hours was ≥82%.

D) Decomposition after 24 and 48 hours was 39 and 61%, respectively.

Table 5 – Oxidation of Nitrogen Compounds by Chlorine
0.25 ppm Nitrogen, Temp. ~22°C

in the absence of sunlight, it decomposes in sunlight resulting in partial oxidation of ammonia nitrogen as shown below (Wojtowicz 1985).

$$NH_2Cl + h\nu \rightarrow 1/3N_2 + 1/3NH_4^+ + 2/3H^+ + Cl^-$$
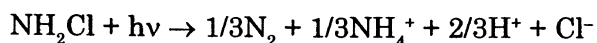
Where $h\nu$ represents a photon of absorbed ultraviolet light. Thus, 2/3 or 67% of the ammonia nitrogen present in the form of monochloramine is oxidized by the above photochemical reaction. In effect, all of the combined chlorine is utilized in oxidation of

ammonia nitrogen. Since di– and trichloramine are much stronger absorbers of ultraviolet light (see Table 4), they should decompose even faster.

Oxidation of Nitrogen Compounds by Chlorine

Table 5 shows some laboratory data on oxidation of nitrogen compounds by av. Cl (Wojtowicz 1985). Ammonia is fairly rapidly oxidized with a

10–min decomposition of 38% at a stoichiometric dose ratio of 1.8. Bromide ion doubled the decomposition rate to 77%. Doubling the dose ratio more than doubled the decomposition to 87%. Higher pH and the presence of cyanuric acid reduced the decomposition rate to a small extent. Amino acids reacted significantly slower with 60–min extents of decomposition in the 35–66% range. Urea and creatinine reacted much slower than the amino acids with 60–min extents of decomposition in only the 7–8% range. Although bromide ion increased the decomposition of urea and amino acids, it had little or no effect on decomposition of creatinine.

Breakpoint Chlorination of Ammonia

Ammonia nitrogen is oxidized by the process of breakpoint chlorination which was discovered in the late 1930's (Griffin and Chamberlain 1941) in attempts to eliminate taste and odors in public water supplies.

Mechanism – The breakpoint curve in Figure 1 shows the change in combined chlorine as a function of increasing doses of chlorine in the absence of sunlight, i.e., under indoor lighting conditions as in a laboratory. Below pH 9 ammonia is present almost exclusively in the form of ammonium ion (NH_4^+) because it reacts with hydrogen ions.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
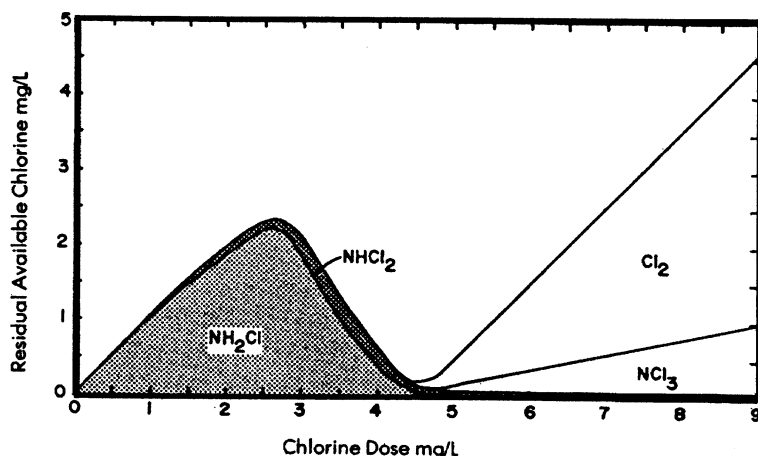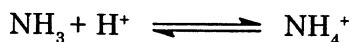
Figure 1 – Breakpoint Chlorination of Ammonia
pH 7.3–7.5, 0.5 ppm Ammonia N, 2–hour Contact Time (Palin 1950)

Ammonium ion rapidly reacts with free available chlorine (i.e., HOCl or ClO⁻) to form monochloramine.

$$NH_4^+ + HOCl \rightleftharpoons NH_2Cl + H^+ + H_2O$$
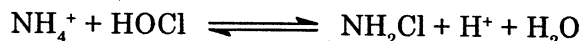
The formation of monochloramine is represented by the line rising diagonally from the origin. At the hump in the breakpoint curve, formation of monochloramine is essentially complete, i.e., each mol of ammonium ion has reacted with approximately one mol of free chlorine forming combined available chlorine (CAC). Beyond the hump of the breakpoint curve, further addition of free chlorine results in formation of dichloramine.

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$
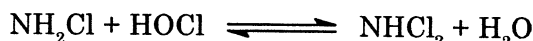
Dichloramine is unstable, its oxidation causes a decrease in CAC, and can be represented by the following reaction:

$$2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3H^+ + 3Cl^-$$
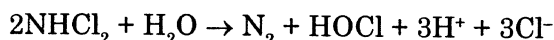
At breakpoint, i.e., the dip in the breakpoint curve, oxidation of ammonium ion (and CAC) is essentially complete. The overall breakpoint reaction is as follows:

$$2NH_4^+ + 3HOCl \rightarrow N_2 + 5H^+ + 3Cl^- + 3H_2O$$
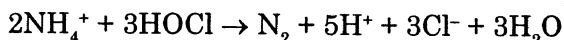
Some oxidation to nitrate ion also occurs by the following overall reaction:

$$NH_4^+ + 4HOCl \rightarrow 6H^+ + NO_3^- + 4Cl^- + 3H_2O$$
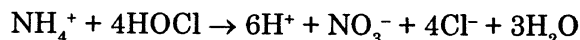
The formation of nitrate ion increases the molar breakpoint chlorine demand per mol of ammonium ion above the theoretical value of 1.5. The actual ratio varies with the excess free chlorine added. It also varies with pH, e.g., 1.88, 1.62, and 1.68 at pH 6.1, 7, and 8 (Palin 1950). Thus, nitrate ion formation can account for 5 to 15% of the breakpoint chlorine demand of ammonia over the 6–8 pH range.

Nitrogen trichloride is formed in significant amounts only past breakpoint, i.e., at higher chlorine doses.

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$
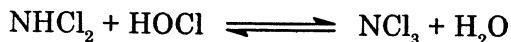
Since nitrogen trichloride is fairly volatile (similar to chloroform), it will tend to volatilize into the atmosphere, thereby reducing the concentration in the water. This will be most pronounced in spas with their higher temperatures and use of aeration. Nitrogen trichloride is also decomposed by sunlight and it can undergo slow decomposition by hydroxide ion enhanced hydrolysis back to $NHCl_2$. The dichloramine that is reformed will decompose by the breakpoint mechanism.

The actual breakpoint chemistry of ammonia is very complex involving no less than 14 reactions (Jafvert 1985).

Chlorine Dosage – The two overall reactions in the breakpoint chlorination of ammonia nitrogen are oxidation to molecular nitrogen and nitrate ion with av. Cl to ammonia mol ratios of 1.5 and 4.0 to one, respectively. Typically about 90% of the ammonia is oxidized to nitrogen and about 10% to nitrate. Thus the average av. Cl to ammonia mol ratio is 1.75 compared to the theoretical 1.5. The chlorine dosage can be calculated from the equation:

$$c = n(71/14)r$$

Where:

c = av. Cl dose (ppm)

n = ammonia nitrogen (ppm)

r = av. Cl/NH₃ molar dose ratio

71 = molecular weight of chlorine

14 = molecular weight of ammonia nitrogen

For the theoretical r value of 1.5, the chlorine

pH	tc (min·ppm)
7.0	250
7.5	140
8.0	270
8.5	740
9.0	1750

Table 6 – TC Values As A Function of pH
15–20°C, n = 0.9–5 ppm, r = 1.6–2.8

dose is 7.6 ppm/ppm ammonia nitrogen and for the typical actual r value of 1.75, the chlorine dose is 8.9 ppm/ppm ammonia nitrogen. However, ammonia itself is typically not present in a chlorine treated pool, but rather in the form of a chloramine. If it is in the form of monochloramine, then the calculated theoretical and actual chlorine doses are much lower, i.e., 2.5 and 3.8, respectively (see Table in Appendix section C).

Kinetics of Oxidation of Ammonia by Chlorine – The kinetics of breakpoint chlorination of ammonia have been extensively studied (Saunier and Selleck 1979). This study determined the time (t) to 99% reduction in ammonia nitrogen and plotted the product of the time (min) and the chlorine dose (ppm) as a function of pH. The tc product is a minimum at pH 7.5 and increases above and below this pH as shown in Table 6. The lower the value of tc the greater the rate of oxidation of ammonia nitrogen.

The time to 99% oxidation of 0.25 ppm ammonia nitrogen at pH 7.5 (tc = 140 min-ppm) and 15–20°C with no free or combined chlorine present initially using the average value of r of 1.75 is calculated as follows:

n = 0.25 ppm, r = 1.75, c = 2.2 ppm

t = tc/c = 140/2.2 = 64 min

If the ammonia in the above example is already present as monochloramine (equivalent to 1.3 ppm combined chlorine) and a shock treatment dose of 10 ppm av. Cl is added, the time to 99% destruction of ammonia nitrogen is significantly lower as shown below:

n = 0.25 ppm, c = 1.3 + 10 = 11.3 ppm

t = tc/c = 140/11.3 = 12 min

Higher temperatures will increase the oxidation rate, especially in spas.

Effect of Organic Matter on Breakpoint Chlorination – In the presence of significant amounts of organic matter the dip in the breakpoint plot is much less pronounced and is more like a plateau, i.e., it occurs at a higher combined residual chlorine level. Thus, the combined chlorine beyond breakpoint is due to NCl_3 and slower reacting organic chloramines, e.g., chlorinated derivatives of

Compound	Nitrogen ppm	CAC ppm	Calculated Cl Dose, ppm per mol N	Calculated Cl Dose, ppm Actual
Monochloramine	0.044	0.22	3.8	0.17
Urea	0.87	0.00	8.9	7.74
Monochloro–amino acid	0.043	0.22	15.7	0.68
Monochloro–creatinine	0.036	0.18	19.3	0.69
Monochloro–uric acid	0.007	0.04	11.8	0.08
total	1.000	0.66		9.36

Table 7 – Combined Chlorine and Calculated Chlorine Dose for Constituents of Urine Based on 1 ppm Total Nitrogen
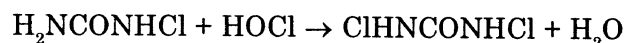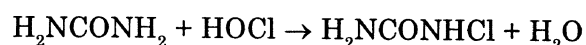
amino acids, creatinine, and other organic nitrogen compounds. Because urea does not form combined chlorine, it will not directly affect the breakpoint curve. Swimming pools typically operate in the region beyond breakpoint, i.e., with free chlorine present, especially during superchlorination (10 times CAC) or shock treatment (e.g., ~ 8 ppm FAC) so that both nitrogen trichloride and organic chloramines will be formed initially.

The presence of organic matter increases the chlorine demand, consequently higher chlorine doses are necessary (see Table in Appendix section C). As mentioned previously, the nitrogen compounds present in swimming pools are due primarily to the release of urine by bathers. Based on the distribution of nitrogen in the main compounds in urine shown in Table 1, the chlorine dose for oxidation of one ppm nitrogen in the form of the constituents of urine is 9.4 ppm assuming only monochloro derivatives are present in the water (Table 7). The total combined chlorine in this example amounts to 0.66 ppm. The NSPI recommends superchlorination (10 times CAC) of the pool water when the CAC exceeds 0.2 ppm (ANSI/NSPI 1992). Thus, the CAC in this example would require 6.6 ppm free chlorine which would not be enough to oxidize all of the bather contaminants if insufficient free chlorine was present.

Oxidation of Urea

Mechanism – Hydrolysis of urea to ammonia and carbon dioxide requires either high temperatures or presence of a catalyst, i.e., the enzyme urease. However, neither of these conditions exist in swimming pools or spas. Thus, the reaction is exceedingly slow in swimming pool and spa water at ordinary temperatures and moderately alkaline pH, and does not occur to a significant extent.

Reaction of free available chlorine with urea can yield a number of chlorinated derivatives (i.e., mono–, di–, tri–, and tetrachloroureas). Solid mono– and dichlorourea derivatives have been prepared (see Wojtowicz 1993).

$$H_2NCONH_2 + HOCl \rightarrow H_2NCONHCl + H_2O$$

$$H_2NCONHCl + HOCl \rightarrow ClHNCONHCl + H_2O$$

$$ClHNCONHCl + HOCl \rightarrow ClHNCONHCl_2 + H_2O$$

$$ClHNCONHCl_2 + HOCl \rightarrow Cl_2NCONCl_2 + H_2O$$
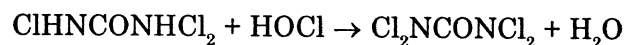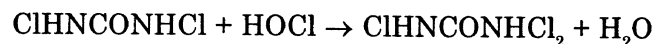
In aqueous solution chloroureas are somewhat unstable. With excess hypochlorite, the reported decomposition products are: CO_2, N_2O, and NCl_3, and NO_3^- (Samples 1959). No reference is made to formation of elemental nitrogen. The proposed mechanism is discussed in the Appendix.

Although urea can form chlorinated compounds in aqueous solution, they apparently readily hydrolyze since they do not contribute significantly to combined chlorine (Palin 1959). In addition, since they do not affect disinfection (Fitzgerald and DerVartanian 1967), their concentration must be quite low. Consequently, the rate of oxidation of urea is slow. For example, at pH 7.2, Palin found that the av. Cl decreased only slightly (from 2.7 to 2.4 ppm) after 24 hours in the presence of 0.5 ppm urea nitrogen.

To the extent that they do form, chlorinated ureas are a source of ammonia chloramines which will be released at a slow rate until all of the urea has been completely oxidized. For example, cleavage of the N–C bond in tetrachlorourea by hypochlorite ion will give one mol of nitrogen trichloride and one mol of dichloramine. The latter can decompose by the breakpoint mechanism. This

Reference	k $(ppm \cdot hr)^{-1}$	Urea Half–Life (hours)
Palin 1950	0.0077	99
Fuchs 1962	0.0161	47
Wojtowicz 1985	0.042	18

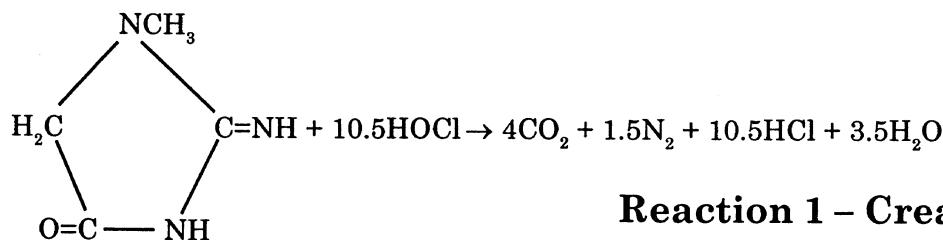**Table 8 – Calculated Urea Half Life in Presence of av. Cl**

mechanism (see alternate mechanism in Appendix A) is consistent with the observation that at pH 8, approximately one mol of nitrogen trichloride was obtained per mol of urea decomposed (Samples 1957).

Kinetics – The kinetics of oxidation of urea by chlorine has been studied (Palin 1950, Fuchs 1985, and Wojtowicz 1985). Analysis of the kinetic data from these studies is discussed in the Appendix B. Table 8 summarizes the kinetic data showing the rate constants and urea half–lifes from these sources.
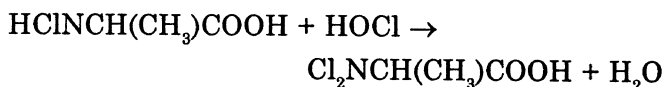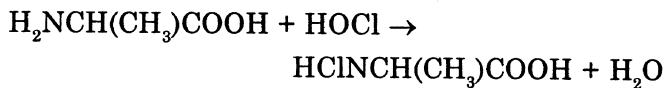
For shock treatment (e.g., 10 ppm FAC) of water containing 1 ppm urea nitrogen, Palin's data indicate a urea half–life of 99 hours, whereas the data of Fuchs indicate a shorter 50% reaction time of 47 hours. By contrast, the data of Wojtowicz indicates an even shorter urea half–life of only 18 hours. If the urea nitrogen and av. Cl concentrations are doubled then the 50% reaction times will be decreased by a factor of two.

Oxidation of Amino Acids

Amino acids contribute to combined chlorine by forming mono– and dichloro derivatives, the relative amounts depending on the ratio of chlorine to amino nitrogen. N–Chloroamino acids are poor disinfectants (Feng 1966). The reactions of free chlorine with alanine are as follows:
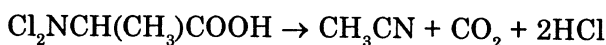
$$H_2NCH(CH_3)COOH + HOCl \rightarrow$$
$$HClNCH(CH_3)COOH + H_2O$$

$$HClNCH(CH_3)COOH + HOCl \rightarrow$$
$$Cl_2NCH(CH_3)COOH + H_2O$$

The monochloro derivative decomposes to acetaldehyde, CO_2, and chloride and ammonium ions (Stanbro and Smith 1979, Alouini and Seux 1988).

$$HClNCH(CH_3)COOH + H_2O \rightarrow$$
$$CH_3CHO + CO_2 + Cl^- + NH_4^+$$
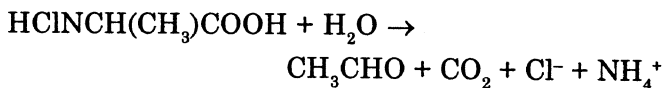
The dichloro compound decomposes to acetonitrile.

$$Cl_2NCH(CH_3)COOH \rightarrow CH_3CN + CO_2 + 2HCl$$

The decomposition of the monochloro derivative is first order with a half–life of 46 min at 25°C over the pH range 5–9. The apparent activation energy is 26.6 Kcal. The acetaldehyde formed will be oxidized by free chlorine to acetic acid ($CH_3CHO + HOCl \rightarrow CH_3COOH + HCl$), whereas the ammonium ion can undergo oxidation to nitrogen by breakpoint chlorination. Hydroxide ion assisted decomposition of N–chloroalalnine can form pyruvic acid ($CH_3COCOOH$). Palin(1950) found that the stability of the N–chloroamino acids decreased in the order: glycine > valine > alanine > tyrosine > cystine.

Acetic and pyruvic acids and acetonitrile can undergo further reactions with free chlorine to chlorinated derivatives. Although the oxidation of alanine by free chlorine resembles breakpoint chlorination, the amount of free chlorine consumed is greater because of oxidation of organic matter.

Oxidation of Creatinine and Creatine

Creatinine is a cyclic compound containing

Reaction 1 – Creatinine

$$\text{(uric acid structure)} \; + 9HOCl \rightarrow 5CO_2 + 2N_2 + 9HCl + 2H_2O$$
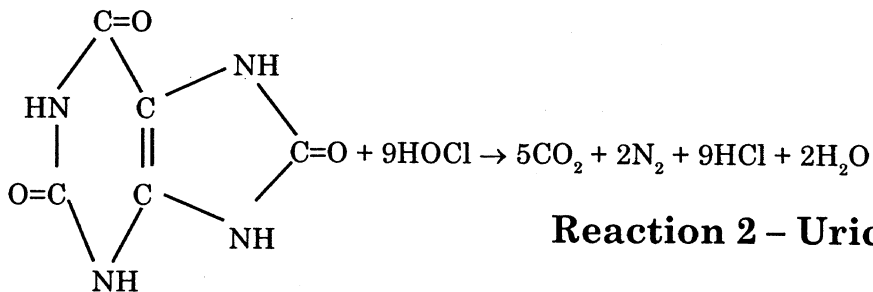
Reaction 2 – Uric Acid

two reactive nitrogen atoms. It forms relatively stable chlorinated derivatives (Lomas 1967) that are decomposed by excess av. Cl (Alouini and R. Seux 1988). Under swimming pool conditions chlorocreatinines decompose very slowly and can persist beyond the breakpoint in oxidation of ammonia and have been characterized as nuisance residuals. Creatinine and creatine (a linear compound $H_2NC(N{=}H)N(CH_3)CH_2COOH$), are closely related compounds. Dehydration of creatine yields creatinine (creatine $\rightarrow$ creatinine $+ H_2O$). Oxidation of creatinine and creatine by excess av. Cl yields carbon dioxide, water, hydrochloric acid, and ammonia chloramines that are then oxidized to nitrogen. The overall reaction for creatinine is shown in Reaction 1.

In the absence of free chlorine, chlorocreatinines can decompose to intermediate products such as: creatinine, creatine, chlorocreatines, and 1–methylhydantoin.

Oxidation of Uric Acid

Uric acid can form mono–, di–, tri–, and terachloro derivatives. With excess chlorine uric acid is oxidized to carbon dioxide, nitrogen, hydrochloric acid, and water. Meso–oxalic acid may form as an intermediate product that can be oxidized to carbon dioxide and water (see Reaction 2).

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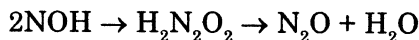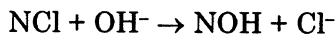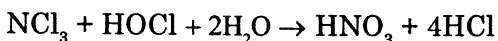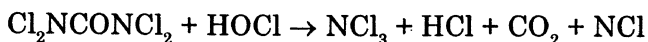
About the Author

Now retired, **Mr. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U. S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 3266 N 151st Drive, Goodyear AZ 85338, phone number 623–535–8851. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide–UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.

Appendix

A. Mechanism of Urea Oxidation by Chlorine

**Proposed Mechanism** – Samples (1959) proposed the following mechanism to explain the products that he observed.

$$Cl_2NCONCl_2 + HOCl \rightarrow NCl_3 + HCl + CO_2 + NCl$$

$$NCl_3 + HOCl + 2H_2O \rightarrow HNO_3 + 4HCl$$

$$NCl + OH^- \rightarrow NOH + Cl^-$$

$$2NOH \rightarrow H_2N_2O_2 \rightarrow N_2O + H_2O$$

Alternate Mechanism – The following mechanism can also explain the products observed by Samples. The carbon–nitrogen bond in chlorinated ureas can be cleaved by hydrolysis or by reaction with av. Cl. For example, reaction of tetrachlorourea with HOCl (or ClO⁻) would give di– and trichloramine.

$$Cl_2NCONCl_2 + HOCl \rightarrow NCl_3 + NHCl_2 + CO_2$$
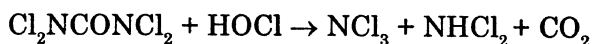
By contrast, cleavage by hydrolysis would give two mols of dichloramine. The dichloramine can decompose by the breakpoint mechanism giving nitrogen and nitrate ion. Formation of nitrate ion can occur as follows:
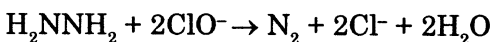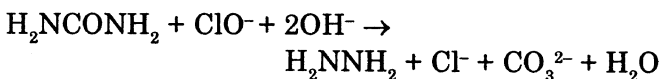
$$NHCl_2 + 2HOCl + H_2O \rightarrow 3H^+ + NO_3^- + 2Cl^-$$
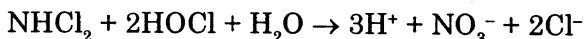
The nitroxyl radical can form by base catalyzed hydrolysis of dichloramine.

$$NHCl_2 + H_2O \rightarrow NOH + 2HCl$$
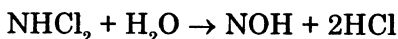
Although the nitroxyl radical might possibly form nitrous oxide as shown above, it can also react with dichloramine (or monochloramine) to form nitrogen.

$$NOH + NHCl_2 \rightarrow N_2 + HCl + H_2O$$
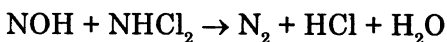
Another potential reaction involves intermediate formation of hydrazine and its oxidation to nitrogen.

$$H_2NCONH_2 + ClO^- + 2OH^- \rightarrow$$
$$H_2NNH_2 + Cl^- + CO_3^{2-} + H_2O$$

$$H_2NNH_2 + 2ClO^- \rightarrow N_2 + 2Cl^- + 2H_2O$$

B. Kinetics of Urea Oxidation by Chlorine

Evaluation of Rate Constant – The instan-

taneous rate of reaction (dx/dt) of urea and chlorine can be represented by a rate constant k times the product of the instantaneous av. Cl and urea N concentrations, where dx and dt are the infinitesimal changes in av. Cl and time. The rate constant k is the rate of reaction at unit concentration of reactants. The reaction is second order, i.e., it depends on the concentration of two reactants.

$$dx/dt = k \text{ [av. Cl] [urea N]}$$

Using Differential Data – The rate of reaction of av. Cl with urea can also be represented using incremental changes in concentration and time by the following equation:

$$\Delta x/\Delta t = k[a][b]$$

where: Δx is the ppm av. Cl reacted in a small time interval Δt, [a] and [b] are the average av. Cl and urea nitrogen concentrations over the time interval Δt, and k is the reaction rate constant. The rate constant k is given by:

$$k = \Delta x \ / \ (\Delta t[a][b])$$

Using the Integrated Kinetic Equation – The rate of consumption of av. Cl by reaction with urea can be represented by the following differential equation, where: dx/dt is the instantaneous rate of av. Cl loss, x is the change in concentration of av. Cl, [a] and [b] are the instantaneous concentrations of av. Cl and urea nitrogen, k is the rate constant, and the incremental amount y of b reacted is related to the av. Cl consumed by $y = x \cdot 14/(71 \cdot 1.75) = 0.113x$.

$$dx/dt = k[a-x][b-y] = k[a-x][b-0.113x]$$

Integration (i.e., conversion of the differential equation to an algebraic equation) and application of boundary conditions (i.e., application of limits) yields the following equation for the rate constant k:

$$k = [2.3/t(0.113a-b)] \text{ Log } [b(a-x)/(a(b-0.113x)]$$

Palin's Data – Kinetic analysis of Palin's data

using the differential equation yields an average value of 0.0080 $(ppm \cdot hr)^{-1}$ for the rate constant. The value of 0.0077 $(ppm \cdot hr)^{-1}$ obtained using the integrated equation compares very favorably with this value.

Under shock treatment conditions, e.g., 10 ppm av. Cl and a urea N of 1.0 ppm, the time to 50% destruction of urea N can be calculated as follows:

$$\Delta x = (0.5 \cdot 71/14) \cdot 1.75 = 4.44 \text{ ppm}$$
$$a = [10 + (10-4.44)]/2 = 7.78 \text{ ppm}$$
$$b = [1 - (1-0.5)]/2 = 0.75 \text{ ppm}$$

Using the differential equation:

$$\Delta t = \Delta x/(k \cdot [a][b]) = 4.44/(0.0077 \cdot 7.78 \cdot 0.75) = 99 \text{ hr}$$

Using the integrated equation:

$$t_{0.5} = [2.3/(k(0.113a-b)] \text{ Log } [b(a-x)/(a(b-0.113x)]$$

$$t_{0.5} = [2.3/(0.0080)(0.113 \cdot 10 - 1)] \text{ Log}[1(10-4.44)/(10(1-0.5)] = 102 \text{ hr}$$

The agreement between the two calculations is excellent.

Data of Fuchs – Analysis of the data of Fuchs gives a higher rate constant of 0.016 $(ppm \cdot hr)^{-1}$ which results in a lower calculated half–life of 54 hours using the integrated equation.

Data of Wojtowicz – Analysis of the data in Table 4 using the differential equation gives an average rate constant of 0.042 $(ppm \cdot hr)^{-1}$. This yields a calculated urea half–life of 18 hours. This value is considerably lower than calculated using the data of Palin or Fuchs.

C. Calculated Chlorine Doses

The Table on the following page shows calculated chlorine doses for oxidation of various nitrogen–containing compounds in swimming pool water.

Compound	Theoretical Dose		Actual Dose	
	Mol Ratio	Av. Cl[D]	Mol Ratio	Av. Cl[D]
	Av. Cl/N	ppm	Av. Cl/N	ppm
Ammonia	1.5	7.6	1.75	8.9
Monochloramine	0.5	2.5	0.75	3.8
Urea	1.5	7.6	1.75	8.9
Amino acid[A]	3.5	17.8	4.1	20.8
Monochloroamino acid[A]	2.5	12.7	3.1	15.7
Dichloroamino acid[B]	0	0	0	0
Creatinine[C]	3.5	17.8	4.1	20.8
Monochlorocreatinine[C]	3.2	16.1	3.8	19.3
Dichlorocreatinine[C]	2.8	14.4	3.4	17.2

A) Additional chlorine may be consumed by oxidation of the byproduct acetic acid.

B) Additional chlorine may be consumed by oxidation of the byproduct acetonitrile.

C) The data for creatine is similar.

D) Per ppm nitrogen.

Calculated Chlorine Doses for Oxidation of Nitrogen Compounds