# Oxidation of Cyanuric Acid with Hypochlorite

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The oxidation of cyanuric acid with available chlorine was studied in order to determine if excessive levels of cyanuric acid could be reduced by treatment with hypochlorite. This study showed that prohibitively high concentrations of available chlorine would be required to achieve significant reductions in cyanuric acid levels in a practical time. The study also indicates that the cyanuric acid loss rate under typical swimming pool conditions is probably not significant.

Experimental

The overall oxidation of cyanuric acid (CA) with hypochlorite ion can be represented by the following reaction:

$$2(HNCO)_3 + 9ClO^- \rightarrow 3N_2 + 6CO_2 + 9Cl^- + 3H_2O$$
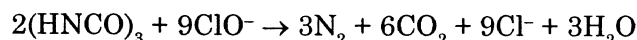
Reactions between cyanuric acid and available chlorine (av. Cl added as hypochlorite) were carried-out under laboratory conditions at 20 to 25°C using a two–liter, 3–neck flask fitted with a stirrer, a pH probe, and burette. Solutions of CA were prepared in dechlorinated tap water. To this solution was added the appropriate amount of 5% NaOCl solution, the pH was quickly adjusted to the appropriate value, and the final volume diluted to 2 liters. A sample was immediately taken for av. Cl analysis and the remainder of this solution was transferred to the reactor described above for kinetic measure-

ments. Since the evolved carbon dioxide forms small equilibrium concentrations of carbonic acid it decreases the pH. The pH was restored to its initial value by addition of standard sodium hydroxide solution forming bicarbonate and carbonate ions.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
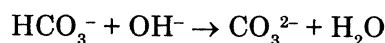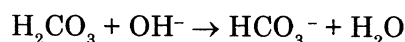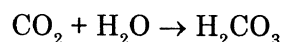
The quantity of cyanuric acid decomposed could be calculated from the volume of sodium hydroxide solution added. Aliquots (250 mL), withdrawn at appropriate times intervals, were analyzed for available chlorine by addition of potassium iodide solution, acidification, and titration of the liberated iodine with standard sodium thiosulfate solution. The data are summarized in Tables 1, 2, and 3.

Discussion

Mechanism

Figure 1 shows the various ionic and hydro-

pH	Oxidation Rate %/hr
7.5	8
9.5	25

Table 1 – Oxidation of Cyanuric Acid by Av. Cl
CA 1714 ppm, Av. Cl 4574 ppm

CA ppm	Time (h)	mL Na₂S₂O₃(V) N=0.02 [A]	Av. Cl [B] ppm	a/(a - x)	k hour⁻¹
1714	0	40.30	572.26	1	
	0.5	39.30	558.06	1.025	
	2.6	38.04	540.17	1.059	
	8.5	34.55	490.61	1.166	
	14.7	31.45	446.59	1.261	0.0163
171.8	0	20.65	58.65	1	
	5	18.40	52.26	1.122	
	12	16.80	47.71	1.229	
	28	14.05	39.90	1.47	
	46	10.80	30.67	1.92	0.0135
85.9	0	10.33	29.34	1	
	7	8.90	25.28	1.161	
	23	7.53	21.39	1.372	
	41	5.70	16.19	1.812	
	63	4.05	11.50	2.551	0.0145
43	0	5.16	14.65	1	
	7	4.40	12.50	1.173	
	23	3.75	10.65	1.376	
	41	2.78	7.90	1.856	
	63	1.95	5.54	2.646	0.0150
21.5	0	2.58	7.33	1	
	7	2.13	6.05	1.211	
	23	1.87	5.31	1.38	
	41	1.43	4.06	1.804	
	63	1.00	2.84	2.58	0.0143
			Average	0.0147	
			Std. Dev.	0.0010	

A.   N = 0.1 in run 1

B.   Av. Cl = VN(0.0355)(10³)/0.25

Table 2 – Oxidation of Cyanuric Acid by Available Chlorine
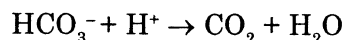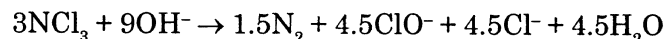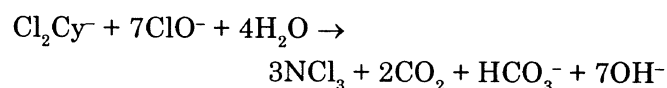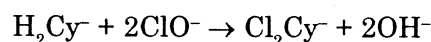
Initial CA ppm	Initial Av. Cl ppm	Rate Constant k h^{-1}	Calc'd. Initial ΔCA ppm/day
1714	571.5	0.0163	74.9
171.8	58.6	0.0135	6.6
85.9*	29.3	0.0145	3.5
43.0	14.7	0.0153	1.8
21.5	7.33	0.0143	0.9
	Average	0.0147	

Table 3 – Decomposition of Cyanuric Acid by Hypochlorite
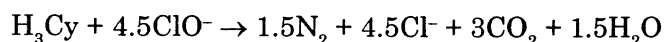**pH 7.5, T = 20–25°C**

lytic equilibria in a cyanuric acid–available chlorine system. A knowledge of all of the equilibrium constants allows calculation of the concentration of individual species as a function pH. The plot in Figure 2 shows calculated species concentrations for water containing 1,714 ppm CA and 4,574 av. Cl. It shows that the dichloroisocyanurate (Cl_2Cy^-) and hypochlorite ions are the main species from a concentration standpoint beyond pH 7.5.

The primary step in decomposition of cyanuric acid by available chlorine involves cleavage of the triazine ring. Cleavage of the triazine ring of isocyanurates is generally believed to involve nucleophilic attack (by a nucleophile) at a carbonyl carbon atom. A nucleophile (e.g., ClO^- or OH^-) is an electron–rich ion or molecule that donates an electron pair to an atom resulting in formation of a covalent bond. It is most likely that the molecule attacked in the ring cleavage reaction is fully chlorinated, i.e., dichloroisocyanurate ion. Ring opening followed by reaction with av. Cl would yield N_2, Cl, CO_2, and H_2O via intermediate formation of NCl_3 as shown below. Studies on decomposition of sodium dichloroisocyanurate solutions showed that it's decomposition was first order with respect to av. Cl, increased with pH, and also involved intermediate formation of NCl_3. The following sequence of reactions is believed to represent the main features of the oxidation of CA by av. Cl.
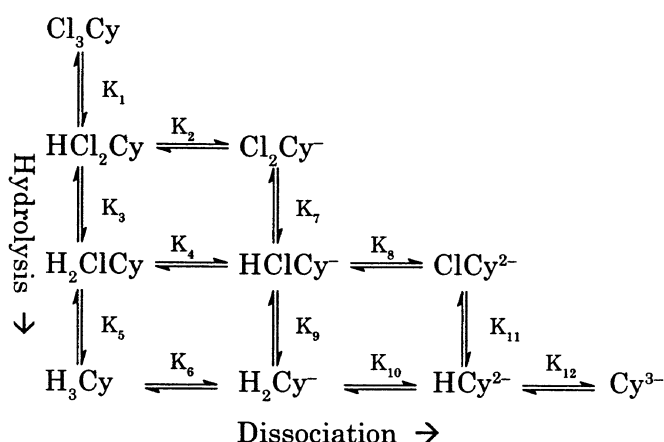
$$H_3Cy \rightarrow H_2Cy^- + H^+$$

$$H_2Cy^- + 2ClO^- \rightarrow Cl_2Cy^- + 2OH^-$$

$$Cl_2Cy^- + 7ClO^- + 4H_2O \rightarrow$$
$$3NCl_3 + 2CO_2 + HCO_3^- + 7OH^-$$

$$3NCl_3 + 9OH^- \rightarrow 1.5N_2 + 4.5ClO^- + 4.5Cl^- + 4.5H_2O$$

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

Overall:

$$H_3Cy + 4.5ClO^- \rightarrow 1.5N_2 + 4.5Cl^- + 3CO_2 + 1.5H_2O$$
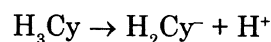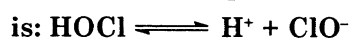
Stoichiometric Reaction

The oxidation of cyanuric acid was initially carried–out using a slight excess of available chlorine over the stoiochimetric molar ratio of avail-

Figure 1 – Equilibria Among Cyanuric Acid and its Chlorinated Derivatives*
*an additional equilibrium
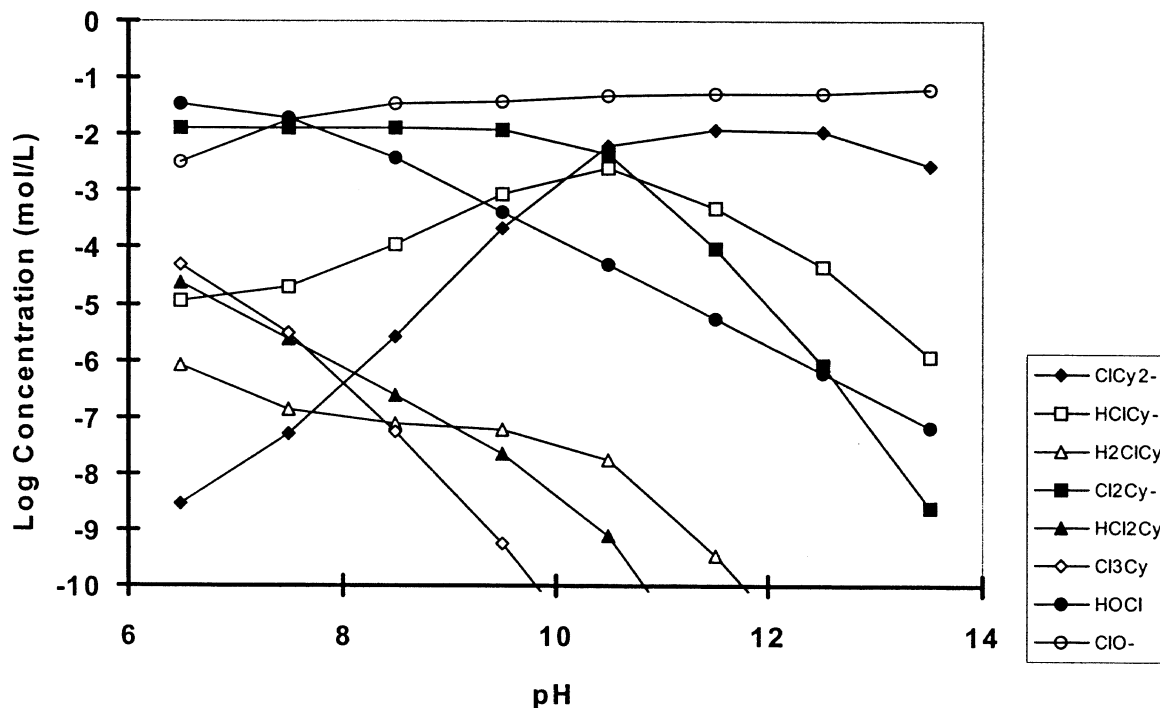is: $HOCl \rightleftharpoons H^+ + ClO^-$

Figure 2 – Species Distribution in the CA/Av. Cl System

able chlorine to cyanuric acid, i.e., 4.9 vs. 4.5. The reaction was shown to be first order (i.e., a linear function) with respect to the cyanuric acid and available chlorine concentrations. The data in Table 1 show that cyanuric acid is oxidized at an initial rate of ~8%/hour at pH 7.5 and threefold faster at pH 9.5.

Whereas the dichloroisocyanurate ion concentration remains essentially constant, the concentration of hypochlorite ion increases twofold over the 7.5 to 9.5 pH range. This can explain most of the increase in the decomposition rate of cyanuric acid over the same pH range. Figure 2 shows that the concentration of dichloroisocyanurate ion decreases beyond pH 9.5 so that if the assumed mechanism is correct, the initial rate of decomposition of cyanuric acid should decrease beyond that pH. This has been observed (Carlson 1978).

The effect of temperature was studied by Carlson (1978) over the 12 to 35°C range at pH 9.5 and a 4.8 NaOCl/CA molar ratio; initial CA concentration was 1714 ppm. Analysis of his data indicates an activation energy of 10,934 calories, which means that the reaction rate approximately doubles for each 10°C rise in temperature.

Substoichiometric Reaction

An eight–fold reduction in the mol ratio av. Cl/

CA (from 4.9 to 0.6) resulted in a 15–fold decrease (from 8.6 to 0.6%/h) in the initial cyanuric acid decomposition rate at pH 7.5. Additional experiments showed that further reductions in concentration at a constant av. Cl/CA molar ratio equal to 0.6 produced a linear decrease in the cyanuric acid decomposition rate and gave reproducible rate constants over an 80–fold concentration range as shown in Table 3.

Kinetics – The rate of oxidation of CA is related to the loss of av. Cl by the following equation:

1. $dCA/dt = (1/4.5)d(av. Cl)/dt$

The rate of consumption of av. Cl is given by the following equation:

2. $d(av. Cl)/dt = k[av. Cl]$

If the av. Cl concentration is equal to $(a - x)$, where a is the initial concentration and x is the amount that has decomposed, equation 2 becomes:

3. $-dx/dt = k(a-x)$

Where: a is the initial concentration of av. Cl, x is

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the amount that has decomposed, and k is a specific reaction rate constant (i.e., the rate of reaction at unit concentration of av. Cl). dx and dt are differentials, i.e., infinitesimal changes in x (the hypochlorite ion concentration) and t (time). Integration (i.e., conversion of the differential equation to an algebraic equation by a process of summation) and application of boundary conditions (i.e., placing limits on the value of x at time 0 and time t) gives the following equation for the loss of available chlorine (x) with time (t) as a function of the initial concentration of available chlorine (a) at pH 7.5 and a ppm CA/ppm av. Cl ratio of 3.0.

4. $\text{Log}\left[a/(a-x)\right] = 0.4343kt$

Equation 4 is of the form $y = mx$. Data and values of $a/(a-x)$ for all experiments are shown in Table 2. A plot of Log $[a/(a-x)]$ against time (Figure 3) should give a straight line with a slope m equal to 0.4343k. Dividing the actual slope by 0.4343 yields the value of k. The average value of k is $0.0147 \pm 0.0010\ \text{h}^{-1}$.

Raising both sides of equation 4 to the power of ten, and since $x = \Delta$ av. Cl (where Δ represents a change in concentration) and $a = [\text{av. Cl}]_i$, this equation can be rearranged to:

5. $\Delta\text{ av. Cl} = [\text{av. Cl}]_i(1 - 10^{-0.4343kt})$

This equation can be converted to an equation for loss of cyanuric acid by substituting the following expression: $\Delta\text{av. Cl} = (\Delta CA \cdot 71 \cdot 4.5)/129$

6. $\Delta CA = 0.404[\text{av. Cl}]_i(1 - 10^{-0.4343kt})$

Substitution of the available chlorine concentration and the time in days gives the cyanuric acid decomposition rate. A summary of the rate constant data and calculated values of the initial cyanuric acid decomposition rate are shown in Table 3.

An equation for calculating the CA decomposition rate at a relatively steady average av. Cl concentration can be obtained by a modification of equation 1:

7. $\Delta CA = 0.404k[\text{av. Cl}]_{\text{AVG}}\Delta t$

Implications for Swimming Pools and Spas – The data in Table 3 show that at a cyanuric acid concentration of 172 ppm and an available chlorine concentration of 59 ppm, that the initial cyanuric acid decomposition rate is only about 7 ppm/day at 20–25°C. The effect of temperature on the cyanuric acid decomposition rate can be calculated by means of the following equation:

8. $\text{Log}\ (R_2/R_1) = 2389(1/T_1 - 1/T_2)$

where R_1 and R_2 are the cyanuric acid decomposition rates at absolute temperatures T_1 and T_2. At a
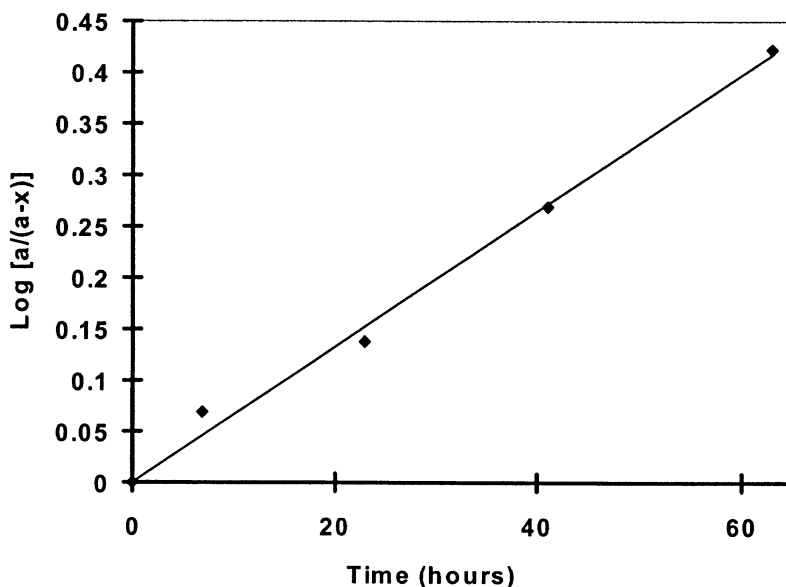

Figure 3 – First Order Plot for Reaction of CA with Av. Cl.

swimming pool temperature of 80°F (i.e., 26.6°C) cyanuric acid decomposition rate would be approximately 1.3 times greater, while at a spa temperature of 104°F (40°C), it would be 2.8 times greater than shown in Table 3 above.

Even if the cyanuric acid and available chlorine concentrations were doubled to 344 and 118 ppm, the initial decomposition rate would be increased to only 18 and 38 ppm/day for pools and spas, respectively. These initial rates would decrease as the concentrations of cyanuric acid and available chlorine decreased. In order to maintain the initial cyanuric acid decomposition rate one would have to not only replenish the available chlorine that had decomposed in the first day but also add an additional amount to compensate for the reduced rate of reaction caused by the decreased cyanuric acid concentration.

The high available chlorine concentration would present a potential corrosion problem for the pool's recirculation system components and might also bleach vinyl pool liners. Thus, oxidation of cyanuric acid by hypochlorite does not appear to be a practical method for reducing excessive levels of cyanuric acid. Partial replacement of the pool water is a much better alternative.

The effect of sunlight on the rate of reaction has not been studied. If the photochemical decomposition of chlorine caused an equivalent increase in the rate of decomposition of cyanuric acid, then it would be beneficial. If it did not then it would decrease the efficiency of the process.

Equations 6 or 7 may not accurately predict the decomposition rate of CA under typical swimming pool conditions (i.e., 80°F and 1 to 3 ppm av. Cl) because the av. Cl/CA mol ratio is much lower (i.e., 0.6 vs. <0.1). The actual loss rate for an average of 2 ppm of av. Cl will be less than the value of 0.24 ppm per day, calculated using equation 6.

References

Carlson, R. H., "Sodium Hypochlorite Treatment for the Removal of Cyanurate Compounds from Aqueous Waste Streams", U. S. Patent 4,075,094 (Feb. 23, 1978) to FMC Corporation.

Wojtowicz, J.A. unpublished data 1981

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.