Reevaluation of Chloroisocyanurate Hydrolysis Constants

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In the course of correlating disinfection data with concentrations of biocidal species in aqueous chlorisocyanurate media, it was necessary to compare and assess the various published values of two of the more important equilibrium constants and their temperature dependence, i.e., the hydrolysis constants of mono- and dichloroisocyanurate ions (Wojtowicz 1996). Data from four sources were analyzed, recalculated, or corrected. Three of these, based on spectrophotometric measurements, gave reasonably consistent values for the hydrolysis constants of mono- and dichloroisocyanurate ions (Brady et al 1963, Gardner 1973, O'Brien et al 1974). Data obtained by polarographic measurement of free available chlorine in aqueous sodium dichloroisocyanurate (Pinsky and Hu 1981) was recalculated using more appropriate models resulting in new values for the hydrolysis equilibrium constants and temperature dependence for mono- and dichloroisocyanurate ions. However, the hydrolysis constants are significantly higher than those reported by others. The reported equilibrium constant for hydrolysis of the dichloroisocyanurate ion obtained by measurement of free available chlorine in aqueous sodium dichlroisocyanurate with added cyanuric acid (Pinsky and Hu 1981) was shown to be erroneous because an incorrect model was employed. In addition, the data appear flawed.

INTRODUCTION

Cyanuric acid – available chlorine aqueous solutions form a complex equilibrium system consisting of seven ionization (including dissociation of HOCl) and 6 hydrolysis reactions (Figure 1). These equilibria are important in applications such as disinfection, sanitization, and bleaching. The most comprehensive study of this system (O'Brien *et al* 1974) determined all 12 isocyanurate equilibrium constants with good precision.

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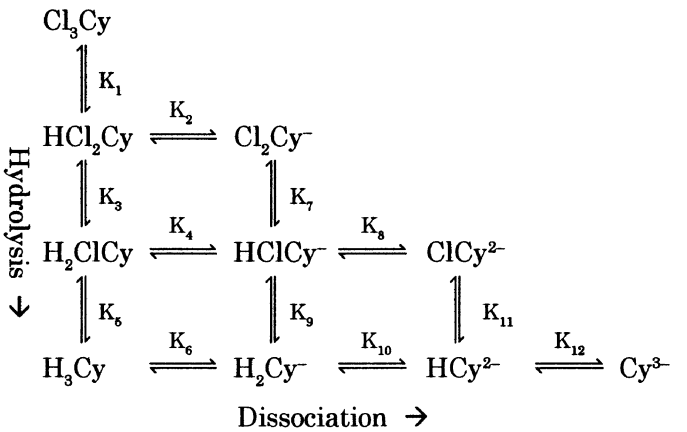

Figure 1 – Chloroisocyanurate Equilibria

The main equilibria in swimming pools, are (where Cy represents the triisocynaurate anion):

1. $Cl_2Cy^- + H_2O \rightleftharpoons HClCy^- + HOCl$
   $K_7 = [HOCl][HClCy^-]/[Cl_2Cy^-]$

2. $HClCy^- + H_2O \rightleftharpoons H_2Cy^- + HOCl$
   $K_9 = [HOCl][H_2Cy^-]/[HClCy^-]$

3. $H_3Cy \rightleftharpoons H^+ + H_2Cy^-$
   $K_6 = [H^+][H_2Cy^-]/[H_3Cy]$

4. $HOCl \rightleftharpoons ClO^- + H^+$
   $K_{HOCl} = [H^+][ClO^-]/HOCl$

A summary of values for pK_7 and pK_9 are given in Table 1, where p denotes the negative logarithm of the equilibrium constant and μ is ionic strength. The values of pK_7 and pK_9 reported by Pinsky and Hu (1981) are significantly lower than those from other studies (Brady *et al* 1963, Gardner 1973, O'Brien *et al* 1974). However, Seux *et al* (1984) claim better agree-

ment between calculated and observed hypochlorite ion concentrations using constants of Pinsky and Hu than obtained using values of O'Brien *et al* (1974).

RESULTS AND DISCUSSION

Reevaluation of the Data of Brady *et al* – Values of K_7 and K_9 at pH 9.7 were determined by measuring the ClO^- concentration in millimolar solutions of varying cyanurate and available chlorine concentrations (Brady *et al* 1963). Correction of the data using more reliable values for ionization constants of $HClCy^-$ and H_2Cy^- from O'Brien *et al* (1974), i.e., $pK_8 = 10.08$ and $pK_{10} = 11.4$, gave $pK_7 = 4.50$ and $pK_9 = 5.67$. These values are in excellent agreement with O'Brien's values of $pK_7 = 4.51$ and $pK_9 = 5.62$.

Reevaluation of the Data of Gardner – Gardner (1973) determined K_7 by measuring the ClO^- concentration in millimolar sodium dichloroisocyanurate (SDCC) solutions at pH 7.6–8.6 and K_9 by performing similar measurements at pH 9.3–10.3. Recalculation of the higher pH data using Model C (see Appendix), in conjunction with the currently accepted value for the ionization constant of HOCl (Morris 1966) and values of pK_8 and pK_{10} from O'Brien *et al* (1974), gave $pK_7 = 4.84$ and $pK_9 = 5.72$. The value of pK_7 was obtained by iteration, i.e., it was adjusted using a convergence technique such as Excel Solver, until the standard deviation in pK_9 was minimized. This value of pK_9 is in much better agreement with the O'Brien *et al* value of 5.62 than the reported value of 6.0. Analysis of the lower pH data gave $pK_7 = 4.78$, which is close to the value of 4.84 obtained from analysis of the higher pH data.

Reevaluation of Pinsky and Hu Data on SDCC Solutions – Pinsky and Hu (1981) determined K_9 by measuring the free available chlorine or FAC ($HOCl + ClO^-$) in SDCC solutions. They calculated a value of 5.01 for pK_9 at 25°C using a model which neglects the concentration of Cl_2Cy^-, i.e., they assumed that reaction 1 is essentially complete. However, this is not true for all of their data, especially at lower temperatures and higher concentrations. Analysis of the data using a model which includes Cl_2Cy^- (see Appendix Model A) allows calculation of both pK_7 and pK_9 since hydrolysis of Cl_2Cy^- is incomplete, especially at higher concentrations and lower temperatures. The concentration of cyanurate species can be represented in terms of the total cyanurate, total av. Cl, the measured FAC, and K_7. The value of pK_7 was found by iteration when the standard deviation of pK_9 was minimized. This technique was successful for the data at 15.5 and 25°C, but not at 30°C, due to almost complete hydrolysis of Cl_2Cy^- at the latter temperature as shown in Table 2.

Reference	Method	T °C	μ	pK_7	pK_9
O'Brien *et al*	$pK_3 + pK_4 - pK_2$[a]	24–25	0.02	4.51±0.09	
"	uv[b]	24–25	0.02		5.62±0.05
Brady *et al*	uv[c]	23±2	0.5	4.8	5.4
Gardner	uv[d]	23	0.3	4.85±0.09	6.0±0.15
Pinsky & Hu	voltammetry pH 7.5	22±2	0.2	4.00[e]	
"	"	25	0.2		5.01[f]

a) pK_3 (uv), pK_4 (spectral titration), and pK_2 (electrometric titration).

b) Measurement of ClO^- at pH 9.5 – 10.6.

c) Measurement of ClO^- at pH 9.7 with correction for effects of K_8 and K_{10}.

d) Measurement of ClO^- at pH 7.6 – 8.6 and pH 9.3 – 10.3, respectively.

e) Calculated from alkaline hydrolysis constant ($K_{7a}K_{9a} = 8000$) determined by adding cyanuric acid to a solution of sodium dichloroisocyanurate and K_{9a} determined on aqueous SDCC solutions:

$$K_{7a} = 8000/K_{9a} = 8000/28 = 285.7$$

$$K_7 = K_{7a}K_w/K_{HOCl};\ pK_7 = -\text{Log } 285.7 + pK_w - pK_{HOCl} = -2.46 + 14 - 7.54 = 4.00$$

This value of pK_7 is erroneous as discussed below.

f) Calculated from alkaline hydrolysis constant ($K_{9a} = 28$) determined on solutions of sodium dichloroisocyanurate: $pK_9 = -\text{Log } 28 + 14 - 7.54 = 5.01$

Table 1 – Summary of pK_7 and pK_9 Measurements

Temperature °C	% Hydrolysis[a]
15.5	98–82
25	100–94
30	~100

a. For lowest to highest concentrations.

Table 2 – Hydrolysis of Cl_2Cy^- vs. Temperature

Attempts to minimize the standard deviation of pK_9 at 30°C forced the concentration of Cl_2Cy^- to essentially zero, yielding a value of 4.71 for pK_9, and eliminating the possibility of calculating K_7. An identical value was obtained using a simpler model which neglects Cl_2Cy^- (see Appendix Model B). The results are shown in Tables 3, 4, and 5 and are summarized in Table 6. The new value of pK_9 at 25°C is in good agreement with the Pinsky and Hu value, but the values at 15.5 and 30°C differ significantly. However, at 25°C, the values of pK_7 and pK_9 are considerably lower than other reported values shown in Table 1 (Brady *et al* 1963, Gardner 1973, O'Brien *et al* 1974).

Temp. °C	pK_7	pK_9	
	a	a	Pinsky and Hu
15.5	3.63	5.56±0.08	5.92
25	3.11	4.96±0.05	5.01
30	2.84[c]	4.71±0.10[b]	4.56

a. Based on a model A which includes Cl_2Cy^-.

b. Based on a model B which excludes Cl_2Cy^-.

c. By extrapolation of lower temperature data.

Table 6 – Evaluation of pK_7 and pK_9 from Pinsky's Data on SDCC Solutions

Temperature Dependence of K_7 and K_9 from Pinsky and Hu Data – The temperature dependence of K_7 and K_9 is determined by the heat of reaction (i.e., hydrolysis) which can be calculated via the following relationship: $K_{eq} = Ae^{-\Delta H/RT}$, where: A is a constant, T is the absolute temperature (in kelvins), ΔH is the heat of hydrolysis, and R is the gas constant (8.314 J/mol/deg, 1.987 cal/mol/deg). The values of ΔH shown in Table 7 were obtained by regression analysis of Log K_{eq} against 1/T. The heat of hydrolysis for monochloroisocyanurate ion is significantly lower than the value reported by Pinsky and Hu. This difference is due to the fact that Pinsky and Hu used a model which excluded Cl_2Cy^-. The difference between aqueous and alkaline heats of hydrolysis is due to the fact that the activation energy for the term K_{HOCl}/K_W, which is included in alkaline equilibrium constants, is negative (i.e., ~41,8 kJ/mol, ~–10 kcal/mol). The temperature dependent equations for the aqueous hydrolysis constants K_7 and K_9 are given by:

$$K_7 = 1.09 \cdot 10^{13}\exp(-11{,}078/T)$$

$$K_9 = 2.34 \cdot 10^{12}\exp(-11{,}912/T)$$

Chloro–isocyanurate	Heat of Hydrolysis, kJ/mol (kcal/mol)	
	Aqueous	Alkaline
Cl_2Cy^-, this study	92.0 (22.0)	50.2 (12.0)
$HClCy^-$, this study	99.2 (23.7)	57.3 (13.7)
$HClCy^-$ (Pinsky and Hu 1981)	156.7 (37.6)	115.5 (27.6)

Table 7 – Heat of Hydrolysis of Mono– and Dichloroisocyanurate Ions

Evaluation of K_7 from the Data of Pinsky and Hu on Aqueous SDCC with Added CA – Pinsky and Hu determined K_7 by measuring the change in FAC on addition of cyanuric acid (CA) to an SDCC solution. They used a model which includes Cl_2Cy^-. They found a value of $pK_7K_9 = 9.01$ from which they calculated a value of 4.00 for pK_7. The Pinsky and Hu value for pK_7K_9 is considerably higher than the value of 8.07 found on reevaluation of their data on SDCC solutions. Pinsky and Hu used the following model:

$$K_{7a}K_{9a} = [ClO^- - 2M]^2[H_2Cy^- - M]/\{[Cl_2Cy^- + 2M][OH^-]^2\}$$

An alternate form is:

$$K_7K_9 = [HOCl - 2M]^2[H_2Cy^- - M]/[Cl_2Cy^- + 2M]$$

Where K_{7a} and K_{9a} and K_7 and K_9 are alkaline and aqueous hydrolysis constants, respectively, and M is the molar change in concentration of the respective species upon addition of cyanuric acid. This model indicates that the concentration of Cl_2Cy^- increases with added cyanuric acid. However, this can only occur if $K_7 < K_9$ (i.e., $pK_7 > pK_9$), which is not the case. Indeed, computations using values of $pK_7 = 3.11$ and $pK_9 = 4.96$, calculated from the data of Pinsky and Hu on SDCC solutions, show that the concentration of

Cy_T	Hy	Cl_2Cy^-	H_2Cy^-	$HClCy^-$	pK_9
9.65E–06	1.19E–05	2.04E–07	1.90E–06	6.99E–06	5.73
1.93E–05	2.25E–05	8.00E–07	3.10E–06	1.45E–05	5.56
2.90E–05	3.20E–05	1.76E–06	3.69E–06	2.25E–05	5.52
3.86E–05	4.10E–05	3.03E–06	4.21E–06	3.01E–05	5.48
4.83E–05	4.90E–05	4.61E–06	4.12E–06	3.84E–05	5.52
7.24E–05	6.90E–05	9.58E–06	4.79E–06	5.66E–05	5.48
9.65E–05	8.60E–05	1.59E–05	4.16E–06	7.53E–05	5.56
1.06E–04	9.23E–05	1.87E–05	3.73E–06	8.27E–05	5.62
				Avg.	5.56
				Std. Dev.	0.08
				pK_7	3.63

Table 3 – Evaluation of pK_7 and pK_9 at 15.5°C[a]

Cy_T	Hy	Cl_2Cy^-	H_2Cy^-	$HClCy^-$	pK_9
1.08E–05	1.70E–05	5.15E–08	5.08E–06	4.50E–06	5.00
2.16E–05	3.04E–05	2.52E–07	7.36E–06	1.23E–05	5.02
3.23E–05	4.32E–05	5.89E–07	9.34E–06	2.02E–05	4.98
4.31E–05	5.49E–05	1.08E–06	1.05E–05	2.91E–05	4.99
5.39E–05	6.74E–05	1.68E–06	1.23E–05	3.70E–05	4.93
7.54E–05	9.02E–05	3.28E–06	1.47E–05	5.40E–05	4.89
8.08E–05	9.41E–05	3.80E–06	1.39E–05	5.99E–05	4.94
1.08E–04	1.17E–04	6.74E–06	1.28E–05	8.55E–05	5.04
				Avg.	4.96
				Std. Dev.	0.05
				pK_7	3.11

Table 4 – Evaluation of pK_7 and pK_9 at 25°C[a]

Cy_T	Hy	H_2Cy^-	$HClCy^-$	pK_9
2.23E–05	3.46E–05	1.02E–05	1.00E–05	4.75
2.78E–05	4.12E–05	1.11E–05	1.44E–05	4.80
3.34E–05	4.64E–05	1.07E–05	2.04E–05	4.91
4.45E–05	6.54E–05	1.73E–05	2.36E–05	4.62
5.56E–05	7.59E–05	1.68E–05	3.53E–05	4.74
7.79E–05	1.05E–04	2.24E–05	5.08E–05	4.63
8.35E–05	1.12E–04	2.36E–05	5.50E–05	4.62
9.46E–05	1.25E–04	2.51E–05	6.42E–05	4.61
1.11E–04	1.40E–04	2.40E–05	8.20E–05	4.69
			Avg.	4.71
			Std. Dev.	0.10

Table 5 – Evaluation of pK_9 at 30°C[b]

a. Based on Model B, concentrations in mol/L.

b. Based on Model A, concentrations in mol/L.

	HOCl + ClO^- (ppm)		
Cy_T	Measured	Calculated	
ppm	a	a	b
1.36	1.28	1.25	1.14
3.36	1.04	1.09	0.81
6.36	0.87	0.92	0.54
11.36	0.73	0.78	0.34
21.36	0.60	0.63	0.19
31.36	0.63	0.53	0.13
51.36	0.47	0.43	0.08
61.36	0.52	0.40	0.07
81.36	0.44	0.35	0.05
101.36	0.42	0.34	0.04

a. Values from Pinsky and Hu (1981).

b. Using the model of O'Brien *et al* and substituting values for pK_7 (4.00) and pK_9 (5.01) from Pinsky and Hu (1981).

Table 8 – Comparison of Observed and Calculated FAC

Cl_2Cy^- decreases with added cyanuric acid. Since Cl_2Cy^- is already essentially fully hydrolyzed at 25°C before addition of CA, this eliminates any possibility of determining pK_7. Thus, the reported value of 4.00 for pK_7 is erroneous. The Pinsky and Hu model may be suitable for a single equilibrium reaction, but it cannot be used for two parallel equilibrium reactions.

Pinsky and Hu used the average value of $K_{7a}K_{9a}$ to calculate K_{7a} by using K_{9a} from measurements on SDCC solutions. They apparently overlooked the possibility of calculating K_{7a} directly from the SDCC + CA data, otherwise they would have seen that there was a problem. The consequence of employing the aforementioned incorrect model is revealed when the calculated concentrations of FAC, Cl_2Cy^-, and H_2Cy^- in Table III of the Pinsky and Hu article were used to calculate values of the equilibrium constants (see Table 9). Although the value of $K_{7a}K_{9a}$ is fairly constant, the calculated values of pK_7 and pK_9 are highly variable, the former increasing (from 4.4 to 5.9) and the latter decreasing (from 4.9 to 3.2) with added CA. The fact that pK_7 is larger than pK_9 is a consequence of an incorrect model which requires that the concentration of Cl_2Cy^- increases with added CA. Note that the concentration of $HClCy^-$ hardly changes as the total cyanurate is increased by a factor of 72, which contradicts the expected effect of excess cyanuric acid in repressing hydrolysis.

The incorrectness of the Pinsky and Hu model is further demonstrated by employing their reported constants to calculate the FAC for their experimental data. Using their values of pK_7 (4.00) and pK_9 (5.01), the calculated FAC differs markedly from their calculated values as shown in Table 8. Even if the equilibrium constants obtained from the Pinsky and Hu data on SDCC solutions (i.e., $pK_7 = 3.11$ and $pK_9 = 4.96$) are used, similar low values of FAC are obtained using

CA Added	Cy_T	Hy	Hy	H_2Cy^-	$HClCy^-$	K_9	pK_9
ppm	mol/L	ppm	mol/L	mol/L	mol/L		
0	1.05E-05	1.26	1.78E-05	5.82E-06	3.23E-06	1.72E-05	4.76
2	2.60E-05	1.04	1.47E-05	1.57E-05	6.33E-06	1.96E-05	4.71
5	4.92E-05	0.87	1.23E-05	3.24E-05	8.73E-06	2.45E-05	4.61
10	8.80E-05	0.73	1.03E-05	6.18E-05	1.07E-05	3.19E-05	4.50
20	1.65E-04	0.60	8.46E-06	1.22E-04	1.25E-05	4.43E-05	4.35
30	2.43E-04	0.63	8.82E-06	1.85E-04	1.22E-05	7.17E-05	4.14
50	3.98E-04	0.47	6.63E-06	3.07E-04	1.44E-05	7.60E-05	4.12
60	4.75E-04	0.52	7.33E-06	3.69E-04	1.37E-05	1.06E-04	3.97
80	6.30E-04	0.44	6.21E-06	4.92E-04	1.48E-05	1.11E-04	3.96
100	7.85E-04	0.42	5.92E-06	6.16E-04	1.51E-05	1.30E-04	3.89

Cy_T = total cyanurate

Hy = HOCl + ClO^-

Table 10 – Evaluation of pK_9 by Addition of Cyanuric Acid to Sodium Dichloroisocyanurate*

*Based on Table III of the Pinsky and Hu paper. Species concentrations calculated using Model B.

CA added	Cy_T	Hy	Hy	Cl_2Cy^-	H_2Cy^-	$HClCy^-$ [b]	$K_{7a}K_{9a}$ [c]	K_9 [d]	pK_9	K_7 [e]	pK_7
ppm	mol	ppm	mol/L	mol/L	mol/L	mol/L					
0	1.05E–05	1.25	1.76E–05	7.40E–07	4.90E–06	3.68E–06	5153	1.17E–05	4.93	4.39E–05	4.36
2	2.60E–05	1.09	1.54E–05	1.30E–06	1.73E–05	3.24E–06	7875	4.10E–05	4.39	1.92E–05	4.72
5	4.92E–05	0.92	1.30E–05	1.90E–06	3.60E–05	2.69E–06	7987	8.68E–05	4.06	9.18E–06	5.04
10	8.80E–05	0.78	1.10E–05	2.40E–06	6.40E–05	6.20E–06	8080	5.68E–05	4.25	1.42E–05	4.85
20	1.65E–04	0.63	8.89E–06	2.90E–06	1.20E–04	1.37E–05	8180	3.89E–05	4.41	2.1E–05	4.68
30	2.43E–04	0.53	7.48E–06	3.30E–06	1.90E–04	3.98E–06	8055	1.79E–04	3.75	4.51E–06	5.35
50	3.98E–04	0.43	6.06E–06	3.60E–06	3.15E–04	3.60E–06	8058	2.66E–04	3.58	3.03E–06	5.52
60	4.75E–04	0.40	5.64E–06	3.70E–06	3.78E–04	2.84E–06	8141	3.76E–04	3.42	2.16E–06	5.67
80	6.30E–04	0.35	4.94E–06	3.90E–06	5.00E–04	6.27E–06	7822	1.97E–04	3.71	3.97E–06	5.40
100	7.85E–04	0.34	4.80E–06	4.00E–06	6.28E–04	2.37E–06	9039	6.34E–04	3.20	1.42E–06	5.85
						Avg.	8137				
						Avg.[f]	7839				

a. Based on data from Table III in the Pinsky and Hu paper.

b. Calculated values: $HClCy^- = Cy_T - 1.24 \cdot H_2Cy^- - Cl_2Cy^-$

c. $K_{7a}K_{9a} = [Hy/2]^2[HClCy^-]/\{[Cl_2Cy^-][OH^-]^2\}$

d. $K_9 = (Hy/2)[H_2Cy^-]/[HClCy^-]$

e. $K_7 = (Hy/2)[HClCy^-]/[Cl_2Cy^-]$

f. Omitting the first value.

Table 9 – Evaluation of K_7 and K_9 from Aqueous SDCC + Added CA[a]

Cl_T mg/L	Cy_T mg/L	pH	Measured Free Cl mg/L	Calculated Free Cl mg/L			
				O'Brien		Pinsky	
				a	b	a	c
50	45.52	11.75	26.7	30.3	45.5	31.7	45.6
40	36.41	11.75	23.8	24.4	37.0	25.4	37.0
30	27.31	11.65	18.4	18.4	27.9	19.1	28.0
20	18.21	11.65	11.5	12.5	19.0	12.8	19.0
10	9.10	12.05	6.1	6.4	9.9	6.4	9.9
50	45.52	8.00	17.2	12.0	11.6	15.5	16.6
40	36.41	8.00	14.5	10.4	10.1	13.2	14.4
30	27.31	8.15	12.2	9.6	9.3	11.7	13.0
20	18.21	8.15	9.3	7.4	7.1	8.6	9.9

a. Calculated values by Seux *et al.*

b. Calculated values by Wojtowicz using equilibrium constants and computer program of O'Brien *et al.*

c. As in (b) except using values of Pinsky and Hu for pK_7 (4.17) and pK_9 (5.01) which correspond to his alkaline hydrolysis constants at ~22°C that Seux *et al* employed: –2.37 (ie, 6.54 – 2.37 = 4.17) and –1.53 (i.e., 6.54 – 1.53 = 5.01), respectively; where $pK_W - pK_{HOCl} = 14.10 - 7.56 = 6.54$.

Table 11 – Analysis of Data of Seux *et al* (1984)

either the O'Brien *et al* model or the simplified model which excludes Cl_2Cy^-. The Pinsky and Hu model also calculates incorrect FAC values using constants from O'Brien *et al* as shown in Fig. 8 of their article. For example, their calculated value of ~0.2 ppm FAC at 30 ppm added CA is much greater than the value of 0.035 ppm calculated using either the O'Brien *et al* model or model B.

Calculation of pK_9 from the data of Pinsky and Hu using a model that excludes Cl_2Cy^- (see Appendix Model B) as a significant species, shows that it varies from 4.8 to 3.9 from the lowest to the highest concentration. Not only is the value of pK_9 highly variable, it is markedly different than their reported value of 5.01 (see Table 10). This is not a concentration effect, since the maximum concentration of total cyanurate is $<10^{-4}$ mol/L. Ionic strength would not be a factor since the activity of HOCl is ~1 and the activity coefficients of H_2Cy^- and $HClCy^-$ will cancel each other, because they are similar and one is in the numerator and the other in the denominator.

The problem appears to lie with the data of Pinsky and Hu. Their measured HOCl + ClO^- values for experiments with added cyanuric acid are much too high, especially at cyanuric acid concentrations employed in swimming pools. They show that the concentration of HOCl + ClO^- is decreased by a factor of only 3.5 as the total cyanurate is increased from 1.4 to 101.4 ppm. This is in conflict with the dramatic stabilizing effect of cyanuric acid which extends the lifetime of av. Cl from ~2–3 hours to several days (Nelson 1967) and the greater than tenfold increase in kill time of bacteria observed over a similar concentration range (Anderson 1965). Possible explanations are: 1) the FAC values are higher than actual or 2) the

	ClO^- mg/L	
pH	Calculated	Found
8.03	52.0	48.9
8.41	66.2	62.4
8.69	76.9	73.0
9.00	90.2	83.0
9.25	102.0	97.1
9.57	117.7	119.1
9.84	129.7	132.6
10.06	137.7	140.4
10.37	145.8	151.0

Table 12. Comparison of Calculated and Experimental Concentrations of ClO^- as a Function of Temperature: Cl_T = 202.1mg/L, Cy_T = 129.1 mg/L Data of O'Brien *et al*

amount of cyanuric acid added is actually less than reported by a factor 5 to 10.

Analysis of Data of Seux *et al* – Seux *et al* (1984) claim better agreement between experimental and calculated HOCl + ClO^- concentrations using K_7 and K_9 values of Pinsky and Hu than with values of O'Brien *et al*. First of all, the calculated values of Seux *et al* (Table 11) for experiments at pH 11.65–12.05 appear to be incorrect, i.e., they are lower by a factor of ~1.5 than calculated by Wojtowicz with the model of O'Brien *et al* using either the O'Brien *et al* or Pinsky and Hu values for K_7 and K_9. This indicates a potential experimental error in the measured av. Cl concentrations. The Wojtowicz calculations show that the O'Brien *et al* and Pinsky and Hu constants yield essentially identical values of HOCl + ClO^-.

At lower pH (8–8.15), the calculated values of Seux *et al* using constants of O'Brien *et al* are in fairly close agreement with calculations of Wojtowicz. However, they are lower by a factor of 1.1 than those of Wojtowicz when using constants of Pinsky and Hu. Although the agreement between calculated and measured values of HOCl + ClO^- at pH 8–8.15 is better using K_7 and K_9 values of Pinsky and Hu than with values of O'Brien *et al*, one must take into account the fact that the Pinsky and Hu value of K_7 is erroneous as previously discussed. If the values of K_7 and K_9 found on reevaluation of the data of Pinsky *et al* (i.e., $pK_7 = 3.11$ and pK_9 4.94) are used, then the agreement is very poor. For example, at pH 8.00 and 50 mg/L av. Cl, the calculated value HOCl + ClO^- is 25.3 mg/L compared to the measured value of 17.2 mg/L.

Data of O'Brien – By contrast with the data of Seux *et al*, O'Brien (1972) found excellent agreement between experimental and calculated values of ClO^- over the pH range 8.0 to 10.4 (see Table 12).

Summary of Reevaluated Data – The recalculated data (Brady *et al* 1963, Gardner 1973, Pinsky and Hu 1981) at 23–25°C are compared with the data from the comprehensive study of O'Brien *et al* (1974) in the Table 13. The agreement in pK_9 for (Brady *et al* 1963, Gardner 1973, O'Brien *et al* 1974) is excellent and that in pK_7 is good. By contrast, the Pinsky and Hu values are significantly lower, especially the value of pK_7.

	pK_7	pK_9
O'Brien *et al*	4.51[a]	
O'Brien *et al*, pH 9.5–10.6		5.62[a]
Brady *et al*, pH 9.7	4.50[b]	5.67[b]
Gardner, pH 7.6–8.6	4.78[b]	
Gardner, pH 9.3–10.3	4.84[b]	5.72[b]
Pinsky and Hu, pH 7.5	3.11[c]	4.94[c]

a. At 24 – 25°C

b. At 23 ± 2°C

c. At 25°C

Table 13 – Summary of Reevaluated Data for pK_7 and pK_9

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About the Author

Now retired, **Mr. Wojtowicz** was a senior con-

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Appendix

Isocyanurate Speciation Model*

This general model assumes that $[H_3Cy]$, $[H_2Cy^-]$, $[HCy^-]$, $[HClCy^-]$, $[ClCy^{2-}]$, $[Cl_2Cy^-]$, $[HOCl]$, and $[ClO^-]$ are the only significant species. Material balance for total av. Cl (Cl_T) and total cyanurate (Cy_T) gives:

1. $Cl_T = [HOCl] + [ClO^-] + [HClCy^-] + [ClCy^{2-}] + 2[Cl_2Cy^-] = Hy + [HClCy^-] + [ClCy^{2-}] + 2[Cl_2Cy^-]$

2. $Cy_T = [H_3Cy] + [H_2Cy^-] + [HCy^-] + [HClCy^-] + [ClCy^{2-}] + [Cl_2Cy^-]$

Setting: $[H_3Cy] = [H_2Cy^-][H^+]/K_6$, $[HCy^-] = K_{10}[H_2Cy^-]/[H^+]$, $[ClCy^{2-}] = K_8[HClCy^-]/[H^+]$ and $[HClCy^-] = K_7[Cl_2Cy^-]/[HOCl]$ and inserting into eqs. 1 and 2 gives:

3. $[Cl_2Cy^-] = (Cl_T - Hy)/\{K_7(1+ K_8/[H^+])\}/[HOCl] +2)$

4. $[H_2Cy^-] = \{Cy_T - [Cl_2Cy^-](1+ K_7(1 + K_8/[H^+]))/[HOCl]\}/(1+[H^+]/K_6 + K_{10}/[H^+])$

The concentration of $[HClCy^-]$ is calculated from the material balance eq. 1 after insertion of the appropriate expression for $ClCy^{2-}$.

5. $[HClCy^-] = (Cl_T - Hy - 2[Cl_2Cy^-])/(1 + K_8/[H^+])$

The equilibrium constant K_9 is calculated from:

6. $K_9 = [HOCl][H_2Cy^-]/[HClCy^-] = [Hy/(1 + K_{HOCl}/[H^+])[H_2Cy^-]/[HClCy^-]$

The correct value of pK_9 is obtained by iterating pK_7 until the standard deviation in pK_9 is minimized.

* The following simplified models are obtained by suitable modification of the above general speciation model.

Model A applies to SDCC solutions at pH < 9 and includes: $[H_3Cy]$, $[H_2Cy^-]$, $[HClCy^-]$, $[Cl_2Cy^-]$, $[HOCl]$, $[ClO^-]$

Model B applies to SDCC solutions with added CA at pH < 9 and includes: $[H_3Cy]$, $[H_2Cy^-]$, $[HClCy^-]$, $[HOCl]$, $[ClO^-]$

Model C applies to SDCC solutions at pH > 9 and includes: $[H_2Cy^-]$, $[HCy^-]$, $[HClCy^-]$, $[ClCy^{2-}]$, $[Cl_2Cy^-]$, $[HOCl]$, $[ClO^-]$