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ALAN J. RUBIN
Associate Professor of Civil Engineering
Water Resources Center
The Ohio State University

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CHAPTER 14

EQUILIBRIA IN AQUEOUS SOLUTIONS OF CHLORINATED ISOCYANURATE

J. E. O'Brien, J. C. Morris, and J. N. Butler*

INTRODUCTION

Cyanuric acid and cyanurates have been used for many years in outdoor swimming pools as stabilizers for active chlorine to prevent its photolytic decomposition. In the absence of such stabilizers, usual concentrations of active chlorine can be completely dissipated in 1-2 hours on a sunny day, whereas in the presence of as little as 25 mg/l (0.0002 *M*) cyanuric acid, residual chlorine may persist for several days as a result of the formation of chlorinated cyanurates. Moreover, chlorinated cyanurates, in addition to acting as stabilizers, exhibit a limited degree of hydrolysis to yield a relatively constant level of germicidally potent, free chlorine. In other words, chlorinated cyanurates may be considered as analogous to a protected reservoir which liberates a small but relatively constant level of free chlorine in accordance with clearly defined principles of chemical equilibrium.

Because of the importance of chlorinated cyanurates and because the equilibria in aqueous chlorine-cyanurate mixtures constitute an interesting and challenging physicochemical system in its own right, studies to elucidate quantitatively the equilibrium situation were felt desirable. Additional information beyond that in the literature was needed to predict accurately the concentrations of free chlorine available for germicidal action as a function of reservoir chlorine, total cyanurate, and pH.

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*J. E. O'Brien, Lawrence Experiment Station, Lawrence, Massachusetts. J. C. Morris and J. N. Butler, Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts.

Thus far two terms have been used, "reservoir chlorine" and "free chlorine." Although their meanings may be apparent, it is preferable that precise definitions be provided. These are as follows: (1) Free chlorine is the sum of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), and (2) Reservoir chlorine is free chlorine plus all chlorinated cyanurate species.

Ordinarily, most of the reservoir chlorine consists of chlorinated cyanurates. Although these provide a readily available source of active chlorine, Andersen[1] has submitted evidence that chlorinated cyanurates, as such, are not particularly germicidal. As a result, the germicidal activity must be borne by the relatively small fraction of free chlorine present at any given time. Since, in general, increase in cyanurate concentration results in decreased free chlorine, the use of large cyanurate concentrations to achieve maximum stability will tend to give inadequate germicidal activity. For the same reason the continual addition of chlorinated cyanurates as a source of chlorine is not recommended since this will lead to build up of cyanurate concentration and consequent repression of the concentration of free chlorine below that necessary for effective germicidal activity.

Analysis of Chlorinated Cyanurate Solutions

Although standard analytical techniques tend to show that there are substantial fractions of free chlorine present in solutions containing excess cyanurate, the actual concentration of free chlorine in chlorinated cyanurate systems is usually only a small percentage of the total reservoir chlorine. Whittle[2] has demonstrated that "wet" chemical methods for estimating free chlorine concentrations include some chlorinated cyanurates as well due to the rapid interconversions of species that occur during analysis.

Because of this ambiguity, reliable estimation of equilibrium concentrations of free chlorine, or, indeed, of any individual species in solutions of chlorine plus cyanurate, either requires a physical measurement that does not disturb the equilibrium or must be computed from known equilibrium constants. Computer programs have been developed that permit computation of all the individual species as a function of reservoir chlorine, total cyanurate, and pH value based on knowledge of the individual acidity and hydrolysis constants in solutions of chlorine plus cyanurate.

The Aqueous Chlorine-Cyanurate System

A member of the symmetrical triazine family, cyanuric acid or isocyanuric acid is systematically designated 2,4,6-trihydroxytriazine. It occurs in both the enol and keto tantomeric forms shown in Figure 14.1. Since there is some uncertainty as to which form predominates in solution, the term "Cy" has been used to represent the cyanurate structure. Thus, H_3Cy is cyanuric acid itself, H_2Cy^- its first ionization product, and H_2ClCy its monochlor derivative.

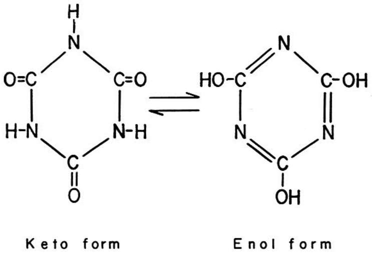

Figure 14.1. Cyanuric acid structure.

Cyanuric acid is a weak tribasic acid that ionizes progressively to H_2Cy^-, $HCy^=$, and $Cy^{\equiv}$. Also, the hydrogens may be successively replaced by unipositive chlorine to give H_2ClCy, HCl_2Cy, and Cl_3Cy. The first two of these compounds also dissociate as acids. As a result solutions of chlorinated cyanurate form a rather complex equilibrium system in which there may be as many as 10 species, regulated in concentration by nine independent equilibrium constants exclusive of the species HOCl, OCl^-, and H_2O, and constants K_{HOCl} and K_w. Some idea of the complexity of aqueous solutions of chlorinated cyanurates can be obtained from Figure 14.2. This is essentially the same illustrative diagram given by Brady, Sancier and Sirine.[3] Assignment of numbers to the equilibrium constants begins with the hydrolysis of trichlorcyanuric acid in the upper left. Ionization processes proceed from left to right and have even-numbered K values (K_2, K_4, etc.). Hydrolytic processes proceed downward and have odd-numbered K values (K_1, K_3, etc.).

In a solution of chlorinated cyanurate, total chlorine concentration is given by the following equation

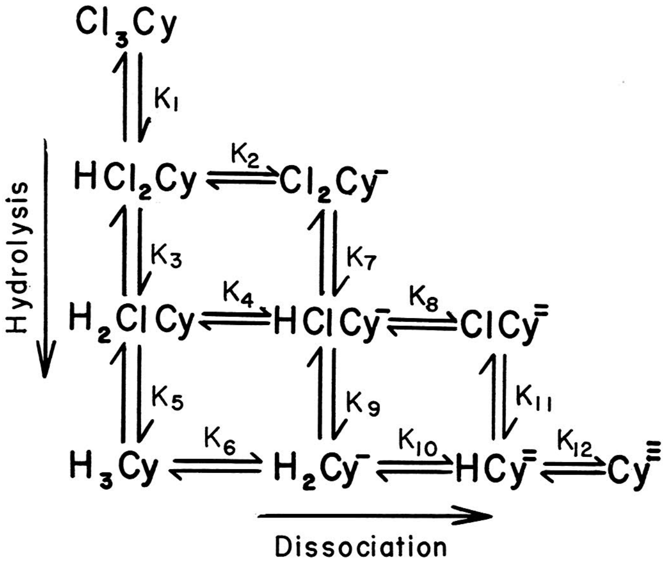

Figure 14.2. Equilibria among cyanuric acid and its chlorinated derivatives.

$$
\begin{aligned}
Cl_T = {} & [H_2ClCy] + [HClCy^-] + [ClCy^=] + [HOCl] \\
& + [OCl^-] + 2[HCl_2Cy] + 2[Cl_2Cy^-] \\
& + 3[Cl_3Cy] \qquad (1)
\end{aligned}
$$

Similarly total cyanurate, Cy_T, is made up as follows

$$
\begin{aligned}
Cy_T = {} & [H_3Cy] + [H_2Cy^-] + [HCy^=] + [Cy^{\equiv}] = [H_2ClCy] \\
& + [HClCy^-] + [ClCy^=] + [HCl_2Cy] \\
& + [Cl_2Cy^-] = [Cl_3Cy] \qquad (2)
\end{aligned}
$$

The concentrations of each species in these equations may be expressed as a function of $[Cy^{\equiv}]$, $[HOCl]$, and $[H^+]$ and the appropriate equilibrium constants shown in

Figure 14.2.* Expressions for the cyanurate species in these terms are:

$$[\text{HCy}^{=}] = \frac{[\text{H}^+][\text{Cy}^{\equiv}]}{K_{12}}$$

$$[\text{H}_2\text{Cy}^-] = \frac{[\text{H}^+]\ [\text{Cy}^{\equiv}]}{K_{12}K_{10}}$$

$$[\text{H}_3\text{Cy}] = \frac{[\text{H}^+]^3[\text{Cy}^{\equiv}]}{K_{12}K_{10}K_6}$$

$$[\text{ClCy}^{=}] = \frac{[\text{H}^+][\text{HOCl}][\text{Cy}^{\equiv}]}{K_{12}K_{11a}}$$

$$[\text{HClCy}^-] = \frac{[\text{H}^+]^2[\text{HOCl}][\text{Cy}^{\equiv}]}{K_{12}K_{11a}K_8} = \frac{[\text{H}^+]^2[\text{HOCl}][\text{Cy}^{\equiv}]}{K_{12}K_{10}K_{9a}}$$

$$[\text{H}_2\text{ClCy}] = \frac{[\text{H}^+]^3[\text{HOCl}][\text{Cy}^{\equiv}]}{K_{12}K_{11a}K_8K_4} = \frac{[\text{H}^+]^3[\text{HOCl}][\text{Cy}^{\equiv}]}{K_{12}K_{10}K_6K_{5a}}$$

$$[\text{Cl}_2\text{Cy}^-] = \frac{[\text{H}^+]^2[\text{HOCl}]^2[\text{Cy}^{\equiv}]}{K_{12}K_{11a}K_8K_{7a}} = \frac{[\text{H}^+]^2[\text{HOCl}]^2[\text{Cy}^{\equiv}]}{K_{12}K_{10}K_{9a}K_{7a}}$$

$$[\text{HCl}_2\text{Cy}] = \frac{[\text{H}^+]^3[\text{HOCl}]^2[\text{Cy}^{\equiv}]}{K_{12}K_{11a}K_8K_{7a}K_2} = \frac{[\text{H}^+]^3[\text{HOCl}]^2[\text{Cy}^{\equiv}]}{K_{12}K_{10}K_6K_{5a}K_{3a}}$$

$$[\text{Cl}_3\text{Cy}] = \frac{[\text{H}^+]^3[\text{HOCl}]^3[\text{Cy}^{\equiv}]}{K_{12}K_{11a}K_8K_{7a}K_2K_{1a}} = \frac{[\text{H}^+]^3[\text{HOCl}]^3[\text{Cy}^{\equiv}]}{K_{12}K_{10}K_6K_{5a}K_{3a}K_{1a}}$$

The molar concentration of any species may be represented as follows

$$[\text{H}_n\text{Cl}_m\text{Cy}] = [\text{H}^+]^{n+m}[\text{HOCl}]^m[\text{Cy}^{\equiv}]\beta_{nm} \tag{3}$$

Both m and the sum of n + m have values running from 0 to 3. The factor, β_{nm}, is equal to the reciprocal of the product of the appropriate equilibrium constants for the species in question. Logarithms of the "beta" values for any species are equal to the sums of the appropriate pK

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*When hydrolytic reactions are considered in the form $\text{XCl} + \text{H}_2\text{O} \rightleftarrows \text{XH} + \text{HOCl}$ instead of the form $\text{XCl} + \text{OH}^- \rightleftarrows \text{XH} + \text{OCl}^-$, then the same numerical suffix given in Figure 14.2 is used for the constant, but the symbol "a" is attached.

values. The expressions for the individual β_{nm} and values for n and m are tabulated in Table 14.I.

Table 14.I

Cyanurate Species Expressed as a Function of [$Cy^{=}$], Number of H Atoms (n), Number of Cl Atoms (m), and the Sum of the Appropriate pK values (log β_{nm})

Species	*n*	*m*	*Log* β_{nm}
[$Cy^{\equiv}$]	0	0	0
[$HCy^{=}$]	1	0	pK_{12}
[H_2Cy^-]	2	0	$pK_{12} + pK_{10}$
[H_3Cy]	3	0	$pK_{12} + pK_{10} + pK_6$
[$ClCy^-$]	0	1	$pK_{12} + pK_{11a}$
[$HClCy^-$]	1	1	$pK_{12} + pK_{11a} + pK_8$ or $pK_{12} + pK_{10} + pK_{9a}$
[H_2ClCy]	2	1	$pK_{12} + pK_{11a} + pK_8 + pK_4$ or $pK_{12} + pK_{10} + pK_6 + pK_{5a}$
[Cl_2Cy^-]	0	2	$pK_{12} + pK_{11a} + pK_8 + pK_{7a}$ or $pK_{12} + pK_{10} + pK_{9a} + pK_{7a}$
[HCl_2Cy]	1	2	$pK_{12} + pK_{11a} + pK_8 + pK_{7a} + pK_2$ or $pK_{12} + pK_{10} + pK_6 + pK_{5a} + pK_{3a}$
[Cl_3Cy]	0	3	$pK_{12} + pK_{11a} + pK_8 + pK_{7a} + pK_2$ $+ pK_{1a}$ or $pK_{12} + pK_{10} + pK_6 + pK_{5a} + pK_{3a}$ $+ pK_{1a}$

One form of the working equation is obtained by substitution in the mass balance

$$\mathrm{Cl_T} = \mathrm{Cy_T}\,\frac{\Sigma\Sigma_m \beta_{nm}[\mathrm{HOCl}]^m[\mathrm{H}^+]^{n+m}}{\Sigma\Sigma\beta_{nm}[\mathrm{HOCl}]^m[\mathrm{H}^+]^{n+m}} + \mathrm{HOCl}\left[1 + \frac{K_{\mathrm{HOCl}}}{[\mathrm{H}^+]}\right] \quad (4)$$

There are ten terms in the denominator of Equation 4 and six terms in the numerator. A computer program that permits calculations based on Equation 4 is given elsewhere.[5] Equation 4 can be used directly with the program to compute the reservoir chlorine required to give any desired level of free chlorine at a specific $\mathrm{Cy_T}$ and pH value. The computation of free chlorine concentration present for a given reservoir value ($\mathrm{Cl_T}$) is more complex. It requires a convergence or iteration technique such as the Newton-Raphson Method.

So, provided the equilibrium K values are accurately known, it is possible to compute results and prepare simplified tables showing the necessary conditions for maintenance of adequate germicidal levels coupled with optimal stabilization of residual chlorine as a function of pH. Later sections of the paper are concerned with the accurate determination of the constants and with a presentation of the results obtained using them.

EXPERIMENTAL APPROACH

Experimental evaluations of K were based primarily on ultraviolet (U.V.) spectrophotometry, *i.e.*, techniques such as differential spectrophotometry and spectrometric titrimetry. Fundamentally the particular measurements performed exploited the often large spectral differences between "adjoining" species such as: (1) cyanuric acid and its successive ionization products; (2) chlorinated cyanuric acids and their successive ionization products; and (3) chlorinated cyanurates and their successive hydrolysis products.

When pH was controlled appropriately and concentrations and ratios of $\mathrm{Cy_T}$ and $\mathrm{Cl_T}$ were selected carefully, it was possible to "isolate" and determine the individual ultraviolet absorption spectrum of nearly every species. It was then possible to devise experiments that would permit determination of nine independent stability constants on the basis of observed spectra of solutions prepared under appropriate conditions and the known values of the molar absorptivities of the individual species. There are potentially ten cyanurate species present at equilibrium. Conditions were chosen, however, to limit the number of significant species present to two or three by selection of pH to control the degree of ionization and by choice of chlorine-cyanurate ratio to repress or encourage hydrolysis. The experimental observations were primarily measurements of absorbance changes accompanying systematic alterations in pH values, total concentration and ratio of cyanurate to chlorine. In addition, some constants were determined by direct electrometric acid-base titration.

An attempt was made to obtain experimental values not only for each of the independent constants, but for some of the redundant constants as well. This provided for independent check on the validity of some of the determinations. Complete details of the experimental measurements can be found elsewhere.[5] All the data used for computation of the molar absorptivities or the equilibrium constants is presented there.

The computer program was of great assistance to the experimental studies. Computed estimates of species' distributions obtained from preliminary values of the equilibrium constants were invaluable for establishment of the conditions and concentrations that would appropriately restrict the number of significant species in subsequent experiments. Reiteration of this procedure eventually permitted selection of conditions and measurement of individual equilibria without strong interference from extraneous processes. Thus, a more accurate determination of many of the constants was possible than had been achieved previously. In some instances errors as great as 0.5 in pK were found for previously determined values.

Importance of Chloride-Free HOCl

Chlorine hydrolyzes in water in accordance with the following equation

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^- \qquad (5)$$

According to Connick and Chia[6] the hydrolysis constant, K, for this reaction is 3.94×10^{-4} at 25° C, where

$$K = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} \qquad (6)$$

At neutral pH and concentrations of chloride ion as great as 10^{-3} *M*, the ratio of $HOCl:Cl_2$ is always greater than 10^6. So, molecular chlorine is essentially absent under such conditions for all practical purposes.

Some of the experimental work in the present study was performed at pH values less than 2, and chlorine concentrations, Cl_T, greater than 10^{-2} *M* were occasionally used. Under these conditions, unless chloride-free HOCl is employed, the ratio of $HOCl:Cl_2$ will be only about 4. Since this condition would have seriously affected equilibria and spectra, chloride-free HOCl was used for all experimental work.

PROCEDURE

The chloride-free HOCl was prepared by neutralizing commercial grade Chlorox with dihydrogen phosphate to a pH of approximately 6, and distilling HOCl under vacuum in a rotary distilling apparatus at 30-35° C. The chlorine concentration of the chloride-free condensate was 0.20-0.23 *M* and, when it was kept in low actinic glass under refrigeration, the solution was stable for several months.

Measurement of Cyanurate Spectra

Previous studies such as the electrometric titrations reported by Monsanto[4] indicated that the first and second ionization constants of H_3Cy and H_2ClCy (K_6 and K_{10}; K_4 and K_8) are separated by more than 4 orders of magnitude. These separations not only permit separation of the unchlorinated species from one another by pH control alone, but also by careful selection of Cy_T and Cl_T concentrations; $Cy_T:Cl_T$ ratios and pH allow isolation of the nonovalent species (H_2Cy^-, $HClCy^-$, and Cl_2Cy^-) and make possible reliable measurement of important portions of their individual spectra.

The chlorinated cyanuric acids can be studied in their undissociated forms at pH values less than 2, for the pK value of the strongest acid (that of HCl_2Cy) is 3.75. Because of the high molar absorptivities of these chlorinated species (1,000-10,000 cm^{-1} 1 mol^{-1}) 0.1-cm light paths and Cy_T concentrations of 10^{-3} to 10^{-2} *M* could be used for spectrophotometric measurements. In this concentration range, hydrolysis of many of the chlorinated species can be effectively repressed by an excess of Cy_T or Cl_T.

As an example, the H_2ClCy spectrum was obtained at pH 2 in the presence of a large excess of Cy_T. If pK_{5a} is approximately 4.0 as estimated by Brady *et al.*,[3] hydrolysis of 10^{-3} *M* H_2ClCy can be completely repressed by 10^{-2} *M* H_3Cy. Read against a blank of 10^{-2} *M* Cy_T, the differential absorbance of H_2ClCy is $A = (e_2 - e_1)bc$, where A is the differential absorbance of H_2ClCy; e_2 and e_1 are the molar absorptivities of H_2ClCy and H_3Cy, cm^{-1} 1 mol^{-1}; b is the light path, cm; and c is the concentration of Cl_T (and H_2ClCy).

The spectra of HCl_2Cy and Cl_3Cy were also obtained at pH 2 in systems with $Cl_T >> Cy_T$. Molar absorptivities at any given wavelength were obtained by plotting absorbance as a function of the reciprocal of the Cl_T:Cy_T ratio and extrapolating to zero. Since Cl_3Cy began forming before HCl_2Cy formation was complete, two linear extrapolations were involved.

The spectrum of slightly hydrolyzed $HClCy^-$ was determined in the presence of a slight excess of H_2Cy^- at a pH value where H_2ClCy and $ClCy^=$ were less than one per cent of the $HClCy^-$ concentration. The total absorbance, read against a water blank, was $A = e_1\ bc_1 + e_2\ bc_2$, where e_1 and e_2 and c_1 and c_2 are, respectively, the molar absorptivities and concentrations of H_2Cy^- and $HClCy^-$ (H_3Cy has no absorbance at the wavelengths examined).

The interesting spectrum of Cl_2Cy^-, a rather widely employed bleach, was readily observed at pH 6 in the presence of excess HOCl.

Spectral determinations were made for eight of the ten cyanurate species (summarized later in Table 14.III). For complete experimental details, reference is made to O'Brien.[5] Conditions did not permit measurement of $Cy^{\equiv}$ and $ClCy^-$ spectra.

Determination of Equilibrium Constants

First Ionization Constant of H_3Cy, K_6

Exploitation of the rather large difference in spectral properties of adjacent or conjugate cyanurate species was one method successfully employed for determining equilibrium constants. A simple example was the spectrometric titration of cyanuric acid to determine its first ionization constant, K_6. Cyanuric acid, H_3Cy, exhibited almost no absorbance at wavelengths longer than 205 nm, whereas its first ion, H_2Cy^-, had an absorbance peak of 8800 cm^{-1} liters mol^{-1} at 214 nm. In order to determine the value for the constant as accurately as possible, one series of experiments measured absorbance as a function of pH at constant Cy_T while another measured absorbance as a function of Cy_T at constant pH.

Second Ionization Constant of H_3Cy, K_{10}

The species H_2Cy^- and $HCy^=$ have overlapping spectra and share an isobestic point at 218 nm. At wavelengths longer than 220 nm, e for $HCy^=$ is much greater than that for H_2Cy^-. Also, at these wavelengths and a light path of 0.1 cm, there is minimal interference from hydroxide ion. Therefore, absorbance as a function of pH at 225 and 230 nm was used to determine pK_{10}.

Third Ionization Constant of H_3Cy, K_{12}

As the pH exceeded 13, absorbance values at wavelengths less than 225 nm (when corrected for OH^- absorbance) showed a slight decrease. Unless this resulted from overcompensation for the large hydroxide absorbance, the third ionization of H_3Cy would appear to have a pK value between 13 and 14.

First Ionization Constant of H_2ClCy, K_4

The experimental determination of the first ionization constant of H_2ClCy was made by a differential spectrometric titration in the presence of excess Cy_T. Sample and blank each contained 0.001 *M* Cl_T and 0.008 *M* Cy_T at an initial pH of 1.8. All subsequent changes in absorbance resulted from increases in pH value. Spectra of the three absorbing species are shown in Figure 14.3 while typical absorbance data are shown in Figure 14.4. Differential absorbance was given by $A = c_1(e_1 - e_3) + e_2c_2$, where e_1, e_2, and e_3 are the molar absorbtivities of $HClCy^-$, H_2Cy^-, and H_2ClCy, respectively, and c_1 and c_2 are the molar concentrations of $HClCy^-$ and H_2Cy^-, respectively.

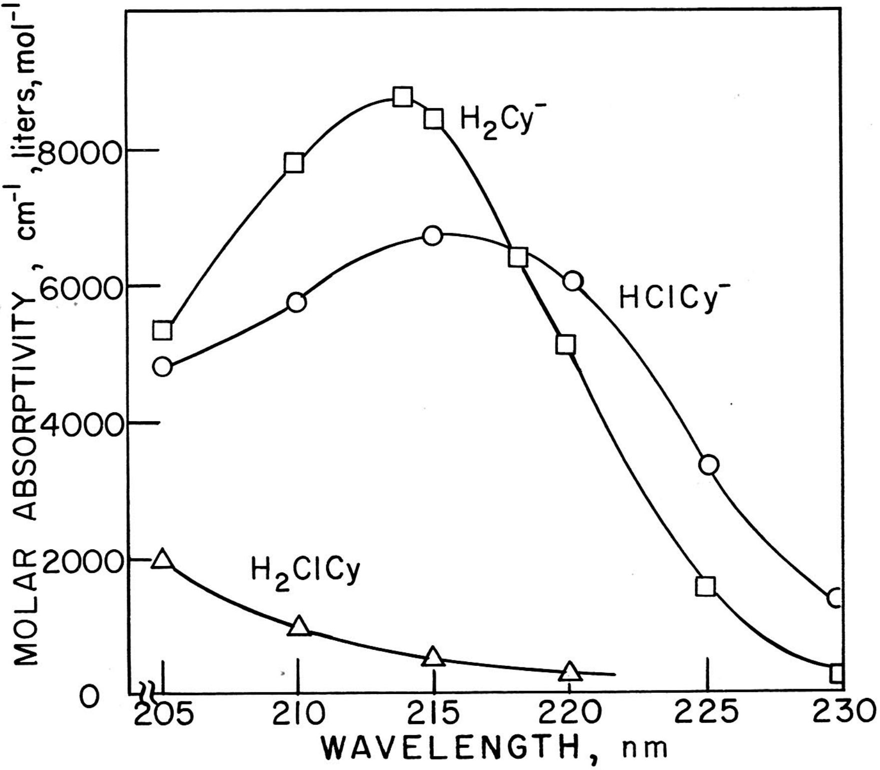

Figure 14.3. U.V. spectra of $HClCy^-$, H_2ClCy, and H_2Cy^-.

Absorbance data between pH values of 4.5 and 5.5 are considered quite significant because formation of $HClCy^-$ was more than half complete within this pH range while interference from H_2Cy^- was still minimal.

Second Ionization Constant of H_2ClCy, K_8

Alkaline hydrolysis of $HClCy^-$ (K_9) was quite extensive in the 10^{-3} *M* range at pH values above 9 and made spectrometric techniques impractical. The method of choice was the electrometric titration of as concentrated a solution as possible with 0.4 *M* NaOH as titrant.

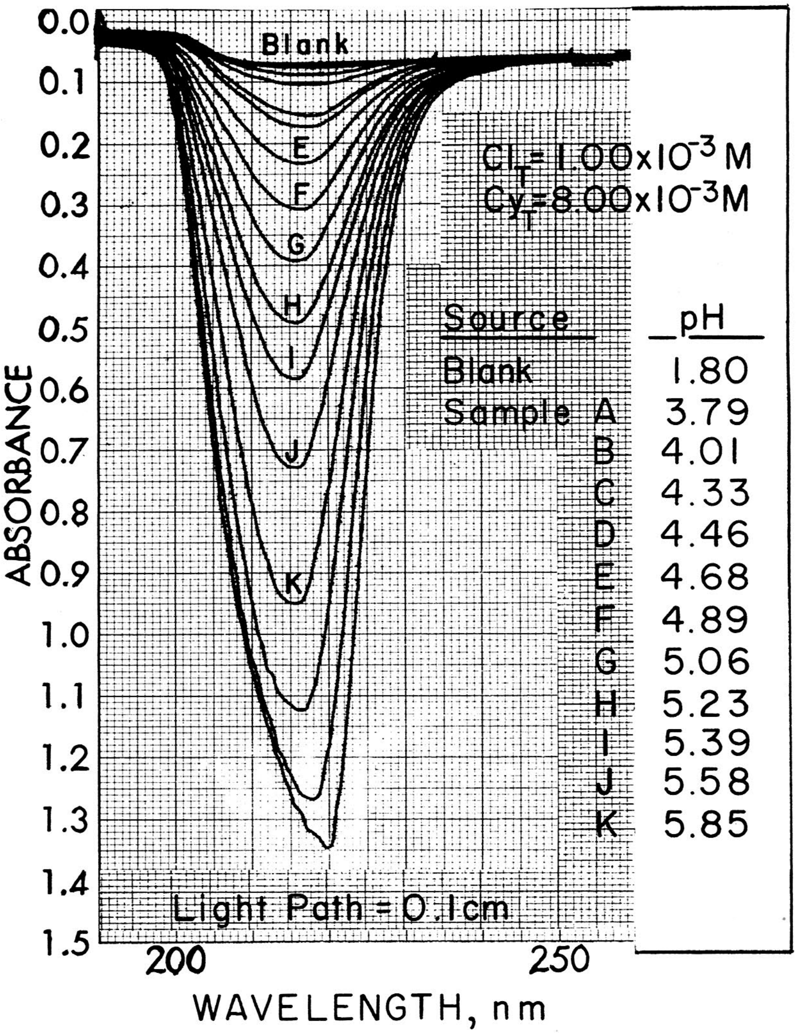

Figure 14.4. Differential absorbance of 10^{-3} M HClCy^{-} as a function of pH.

Ionization Constant of HCl_2Cy, K_2

The experimental value of pK_2 was obtained by an electrometric titration of 10^{-1} *M* Cl_2Cy^- with 1 *M* acid titrant. A 10^{-1} *M* solution is only slightly hydrolyzed at pH values above the equivalence point.

Hydrolysis Constants of Unionized Chlorinated Cyanuric Acids, K_{1a}, K_{3a}, K_{5a}

Cyanuric acid and its chlorinated derivatives are essentially unionized at pH below 1.8. Under these conditions, the number of significant species is reduced to 4 and by careful selection of Cl_T, Cy_T, and Cl_T:Cy_T, this number may be further reduced. Since the successive hydrolysis products of Cl_3Cy have parallel spectra of decreasing absorptivities, hydrolysis is always accompanied by a decrease in absorbance. Changes in absorbance accompanying reciprocal changes in light path and concentration was one technique used to estimate the hydrolysis constants of the chlorinated cyanuric acids. Experiments in this region were handicapped by the close proximity of adjacent hydrolysis constants and limited availability of light in the range at which these compounds absorb energy.

Hydrolysis Constant of Monochlorcyanurate, K_{9a}

Although K_{9a} could have been calculated as a redundant constant ($pK_{9a} = pK_{5a} + pK_6 - pK_4$), experimental estimation of the hydrolysis constant of monochlorcyanurate was desirable because of its importance to chlorine-cyanurate equilibria in environmental systems. The constant actually determined was K_9, the alkaline hydrolysis constant. The reaction for the alkaline hydrolysis of monochlorcyanurate, $HClCy^-$, is as follows:

$$HClCy^- + OH^- = H_2Cy^- + OCl^- \qquad (7)$$

$$K = \frac{[H_2Cy^-][OCl^-]}{[HClCy^-][OH^-]} = K_{9a} \times \frac{K_{HOCl}}{K_w} .$$

The experimental method of choice involved measurement of the U.V. absorption of OCl^- as the pH was varied from

9.4 to 10.6 in a system containing 0.002 *M* Cl_T and 0.003 *M* Cy_T. Experimental determination of K_9 made possible the algebraic computation of K_{5a} and K_{11a} as redundant constants without the necessity of propagating errors through two "equilibrium boxes" (see Figure 14.2). The constant K_{5a} was also estimated experimentally (K_{11a} was not).

RESULTS AND DISCUSSION

Cyanurate Spectra and Stability Constants

Molar absorptivities of the cyanurate species for which spectral determinations were made are listed in Table 14.II.

Experimental values of the equilibrium constants are summarized in Table 14.III. In accordance with Figure 14.2, hydrolysis constants have odd numbers and ionization constants are even-numbered. The table also includes brief comments on experimental methods. When the respective values are placed in their proper location in Figure 14.2, some interesting observations may be made. The addition of each chlorine atom increases constants by 1.4-1.6 orders of magnitude and hydrolysis constants by 1.1 log units (*i.e.*, $HClCy^-$, the chlorinated cyanurate of importance in environmental equilibria, is 40 times less hydrolyzed than its acid). This pattern is consistently observed throughout each of the three "equilibrium boxes" of Figure 14.2.

A summary of results obtained by the Stanford Research Institute[3] and the Inorganic Research Department of Monsanto Chemical Co.[4] are given in Table 14.IV, which also includes those of the present study. In spite of the rather widespread use of cyanuric acid and its chlorinated derivatives, the only values found in the literature for hydrolysis constants were those of the S.R.I. study as reported by Brady, Sancier and Sirine.[3] The Monsanto study determined primarily ionization constants by electrometric titration.

Correlation with Bacteriological Studies

Anderson[1] found that at a pH of 9.0, the addition of 25 mg/l cyanuric acid (1.94×10^{-4} *M* Cy_T) increased the 99 per cent kill time for 0.24 mg/l chlorine (3.40×10^{-6} *M*

Table 14.II

Molar Absorptivities of Cyanurates and Their Chlorinated Derivatives

Species	*196 nm*	*200*	*205*	*210*	*215*	*220*	*225*	*230*
H_3Cy	1830	950	325	155	95	-	-	--
H_2ClCy	3110	2770	1980	960	510	-	-	-
HCl_2Cy	-	-	4030	2900	1710	1310	1060	-
Cl_3Cy	-	-	-	-	3800	3400	2900	2250
H_2Cy^-	-	(3400)	5300	7840	8410	5070	1530	260
$HClCy^-$	-	(4000)	4950	5770	6710	6060	3320	1330
Cl_2Cy^-	-	(8600)	6800	6060	6260	6350	4430	2100
$HCy^=$	-	-	(6000)	5330	5540	6470	5300	2300

Table 14.III

Equilibrium Constants of Cyanurates and Their Chlorinated Derivatives

pK Number	*Method of Determination*	*pK Value*
1a	UV Spectrum at pH<2, $Cl_T >> Cy_T$	1.8 ± 0.2
3a	UV Spectrum at pH<2, $Cl_T > Cy_T$	2.93 ± 0.07
5a	$pK_4 + pK_{9a} - pK_6$	4.07 ± 0.08
(5a)	Differential Spectrophotometry at pH<2, $Cy_T >> Cl_T$	(4.10 ± 0.12)
7a	$pK_{3a} + pK_4 - pK_2$	4.51 ± 0.09
9a*	OCl^- Spectrum during alkaline hydrolysis, $Cy_T > Cl_T$	5.62 ± 0.05
11a	$pK_{9a} + pK_{10} - pK_8$	6.90 ± 0.11
2	Electrometric Titration	3.75 ± 0.03
4	Differential Spectral Titration	5.33 ± 0.05
6	Spectral Titration	6.88 ± 0.04
8	Electrometric Titration	10.12 ± 0.02
10	Spectral Titration	11.40 ± 0.10
12	Spectral Changes at pH 13	13.5

*$pK_9 = -0.84 \pm 0.05$ at 25° C.

$pK_{9a} = pK_w - pK_{HOCl} + pK_9 = 14.00 - 7.54 - 0.84$

$pK_{9a} = 5.62 \pm 0.05$

Table 14.IV

Comparison of Results with Those of Other Investigators

Reaction	*pK No.*	*Present Study*	*Monsanto*[4]	*S.R.I.*[3]
$Cl_3Cy + H_2O = HCl_2Cy + HOCl$	1a	1.8 ± 0.2	--	0.3
$HCl_2Cy = H^+ + Cl_2Cy^-$	2	3.75 ± 0.03	3.95	4.0
$HCl_2Cy + H_2O = H_2ClCy + HOCl$	3a	2.93 ± 0.07	--	3.0
$H_2ClCy = H^+ + HClCy^-$	4	5.33 ± 0.05	5.31	5.7
$H_2ClCy + H_2O = H_3Cy + HOCl$	5a	4.07 ± 0.08	--	4.1
$H_3Cy = H^+ + H_2Cy^-$	6	6.88 ± 0.04	6.93	7.0
$Cl_2Cy^- + H_2O = HClCy^- + HOCl$	7a	4.51 ± 0.09	--	-1.7[a]
$HClCy^- = H^+ + ClCy^-$	8	10.12 ± 0.02	10.09	9.4
$HClCy^- + H_2O = H_2Cy^- + HOCl$	9a	5.62 ± 0.05	--	-1.1[a]
$H_2Cy^- = H^+ + HCy^-$	10	11.40 0.10	11.0	10.6
$ClCy^= + H_2O = HCy^= + HOCl$	11a	6.90 0.11	--	-0.1[a]
$HCy^= = H^+ + Cy^\equiv$	12	13.5		(13)

[a] These values are expressed as alkaline hydrolysis constants. For comparison with the present study a factor of 6.5 should be added to these values (*i.e.* $pK_w - pK_{HOCl}$).

Cl_T) from 3.5 minutes to 15.5 minutes. Utilizing the PPL computer program based on the experimentally determined pK values of the equilibrium model (in which the three master variables are pH, Cy_T, and Cl_T), the computed free chlorine concentration under these conditions was 8.6×10^{-7} *M* or 0.06 mg/l. The ratio of free chlorine in the presence and absence of cyanurate was 0.25:1.00. The ratio of 99 per cent kill-times was 1.00:0.23. Since inactivation-times were almost inversely proportional to free chlorine concentrations, it would appear probable that most, if not all, bactericidal activity resulted from the free chlorine fraction. Although these computations are based on a single comparison, it would seem advisable to regard the chlorinated cyanurate molecule as a free chlorine donor with little bactericidal potency of its own. Any error in this assumption would be in the direction of safety.

Distribution of Individual Species

Examples of computer output based on the equilibrium model are shown graphically in Figures 14.5 and 14.6. In each case the master variables were Cl_T and Cy_T. Molar concentrations of individual species were plotted as a function of pH. Figure 14.5 is intended to depict the distribution of species in a realistic environmental system, *i.e.*, $Cy_T = 2.0 \times 10^{-4}$ *M* (∿25 mg/l), $Cl_T = 2.0 \times 10^{-4}$ *M* (∿1.4 mg/l), and $Cy_T:Cl_T = 10:1$. Figure 14.6 depicts the distribution of individual species in a 10^{-3} *M* solution of $NaCl_2Cy$, a commercial bleach. Between pH values of 3 and 10, 11 of the 12 possible species are present in significant concentrations.

Germicidal responsibility in chlorinated cyanurate solutions is borne principally by the free chlorine fraction. The distribution of free chlorine in three interrelated solutions is summarized graphically in Figure 14.7. All concentrations were computed from the equilibrium system. Symbols were used only for differentiation. Hydrolysis to chlorine is least at a pH of approximately 7.2. The fraction of free chlorine increases rather dramatically at both greater and smaller pH values. At pH values greater than 8, free chlorine exists primarily as the hypochlorite ion. At pH values below 7 free chlorine exists primarily in the form of hypochlorous acid (HOCl) which is approximately 80 times more effective as a bactericide than hypochlorite (OCl^-).

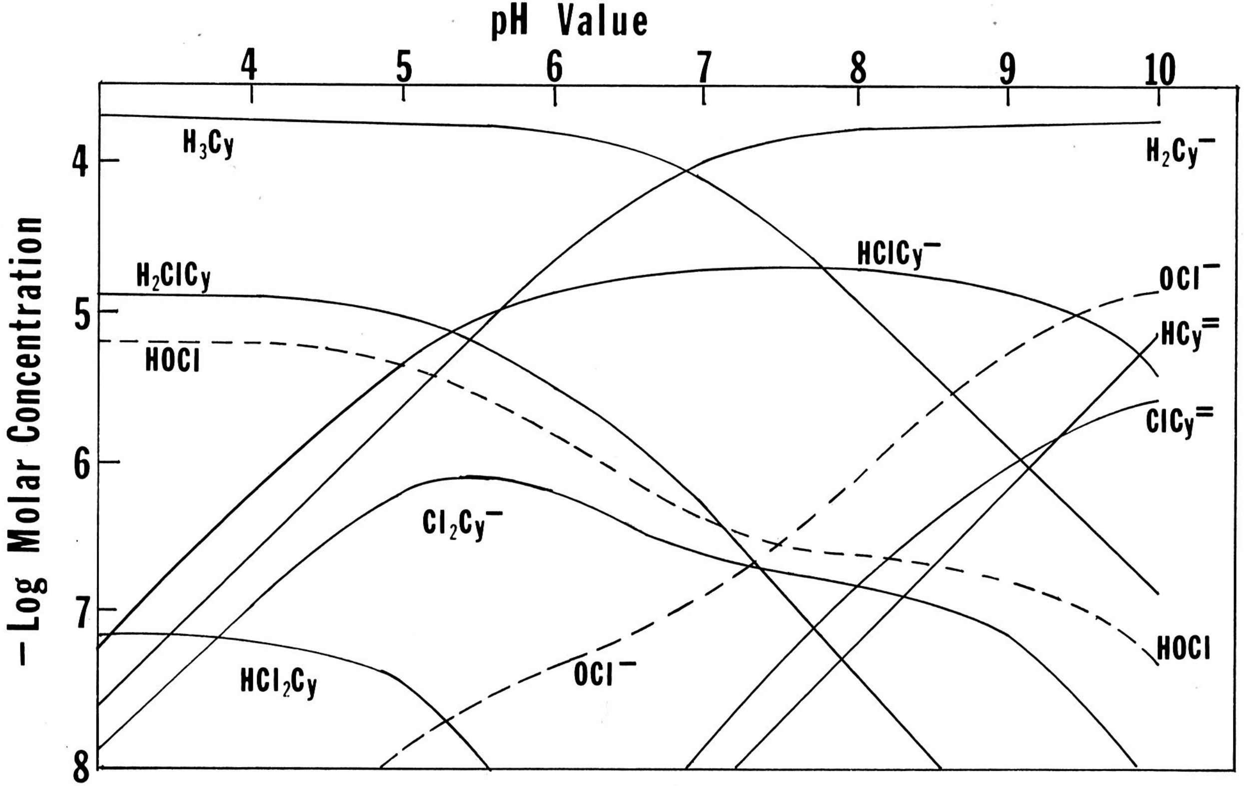

Figure 14.5. Distribution of aqueous chlorine and cyanurate as a function of pH. ($Cy_T:Cl_T$ = 10:1)

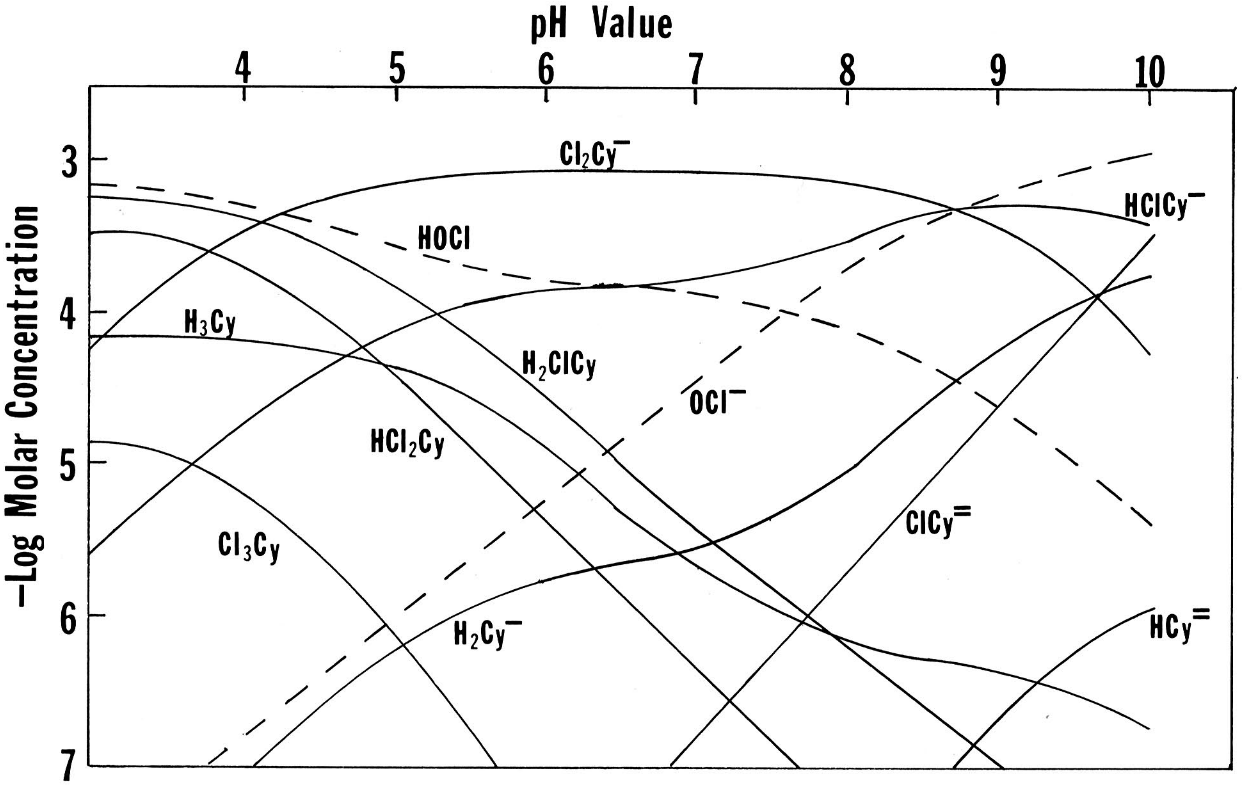

Figure 14.6. Distribution of species for solution of $NaCl_2Cy$ (10^{-3} M).

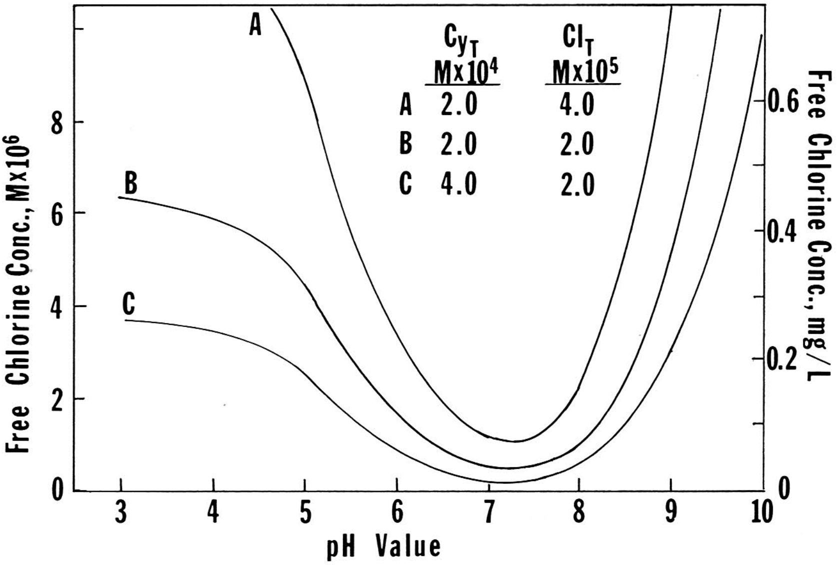

Figure 14.7. Free chlorine as a function of pool pH.

In "environmental" systems such as that depicted in Figure 14.7 (*i.e.*, Cl_T = 1.4-2.8 mg/l and $Cy_T:Cl_T$ = 5.1 to 10:1) free chlorine varies inversely with the total concentration of cyanurate in the neutral pH range (6.0-8.5), indicating that equilibria in such systems is dominated largely by the hydrolysis of monochlor cyanurate ($HClCy^-$).

Figure 14.8 shows the Cl_T concentrations required for desired concentrations of free chlorine (or HOCl) as a function of pH in a system containing a constant Cy_T concentration. It represents the most practical and direct application of the basic computer program to environmental systems.

Photolytic Decomposition of Chlorinated Cyanurate

The effect of sunlight on solutions of cyanuric acid and reservoir chlorine was studied. It would appear that photo-stability is greatest at a pH of about 6.8 and decreases more rapidly at higher pH values than it does at lower pH values. The maximum stability at pH 6.8 accords rather well with the pH of minimum hydrolysis to free

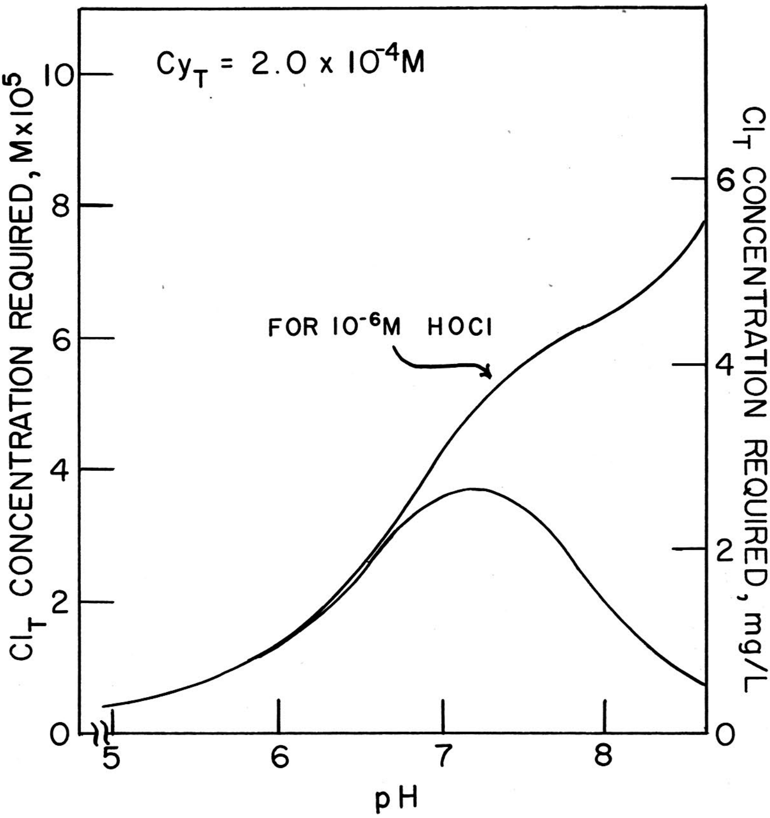

Figure 14.8. *Cl_T required as a function of pH for an equilibrium concentration of 10^{-6} M HOCl or 10^{-6} M $(HOCl + OCl^-)$.*

chlorine; the rapidly increasing instability with increased pH indicates that HOCl has greater stability in sunlight than its ionization product, OCl^-, which has a moderately strong absorptivity in the energy range of sunlight reaching the earth's surface.

Evaluation of Equilibrium Constants

The myriad of changes occurring during alkaline hydrolysis of a chlorinated cyanurate system in which $Cy_T = 10^{-3}$ *M* and $Cl_T:Cy_T > 2$ made it useful as one method of evaluating the experimentally determined equilibrium constants. Consider the reactions occurring in such a system as the pH is gradually increased from 8 to 11:

1. Hydrolysis of dichlorcyanurate:
   $Cl_2Cy^- + OH^- \rightleftarrows HClCy^- + OCl^-$ ($pK_7 = -1.95$)
   (approximately 50 per cent complete at pH 9)
2. Hydrolysis of monochlorcyanurate:
   $HClCy^- + OH^- \rightleftarrows H_2Cy^- + OCl^-$ ($pK_9 = -0.84$)
   (approximately half complete at pH 10.2)
3. Ionization of monochlorcyanurate:
   $HClCy^- \rightleftarrows H^+ + ClCy^=$ ($pK_8 = 10.12$)
   (half complete at pH 10.12)
4. Ionization of H_2Cy^-:
   $H_2Cy^- \rightleftarrows H^+ + HCy^=$ ($pK_{10} = 11.40$
   (approximately 30 per cent complete at pH 11)
5. Hydrolysis of $ClCy^=$:
   $ClCy^= + OH^- \rightleftarrows HCy^= + OCl^-$ ($pK_{11} = 0.44$)
   (approximately 20 per cent complete at pH 11)
6. Ionization of HOCl:
   $HOCl \rightleftarrows H^+ + OCl^-$ ($pK_{HOCl} = 7.54$ at 25° C)

Five equilibria are directly involved in these overlapping reactions and others are indirectly involved. One effect resulting from reactions 1-6 is a gradual increase of hypochlorite ion concentration with increasing pH. It appeared that one method of determining reliability of the equilibrium system was to compare computed values of OCl^- concentrations with those found experimentally. Results of such a comparison are shown in Figure 14.9. Good agreement was attained.

SUMMARY

Wet chemical methods for estimating free chlorine concentrations include chlorinated cyanurates as well. Because of this ambiguity, reliable estimation of equilibrium concentrations of free chlorine, or indeed of any individual species in solutions of chlorine plus cyanurate, either requires a physical measurement that does not disturb the equilibrium or must be computed from known equilibrium constants. A computer program has been developed that permits computation of all individual species as a function of reservoir chlorine, total cyanurate, and pH value based on knowledge of individual

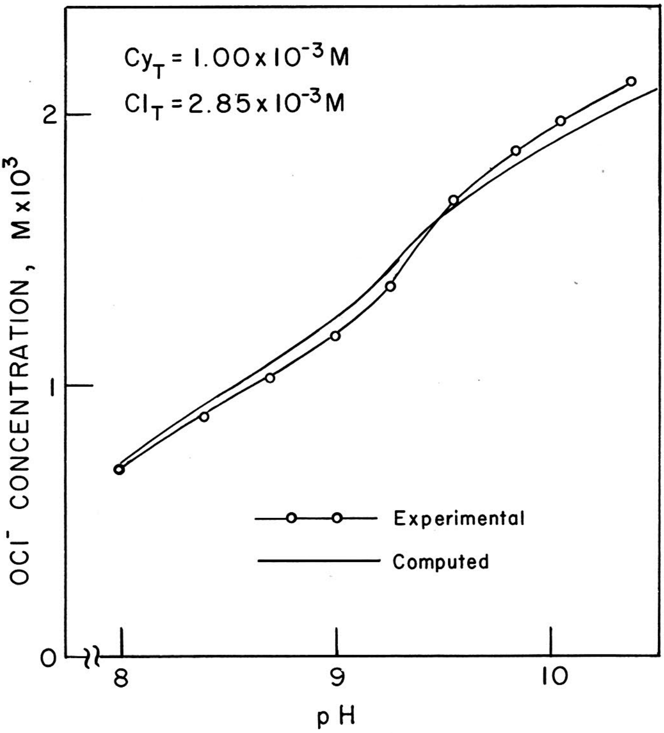

Figure 14.9. Comparison of experimental OCl^- concentrations with theoretical distribution line.

acidity and hydrolysis constants in solutions of chlorine plus cyanurate.

Although chlorinated cyanurates serve as a reservoir of free chlorine, bactericidal efficacy is more closely related to the relatively small fraction of free chlorine present at equilibrium. Therefore, the use of excessive cyanurate in an overly zealous attempt to reduce photolysis may repress free chlorine to the point of suppressing germicidal activity. For the same reason the continual addition of chlorinated cyanurates as a source of chlorine is not recommended because this will lead to build up of cyanurate concentration.

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