3550 Å. (Table IV) is reminiscent of earlier work with iodine–nitromethane[37] and suggests that the naphthalene–chloroform complex is thermodynamically unstable and reacts to form products which would complex with *s*-trinitrobenzene. The new complex(es) would absorb radiation shorter than 3550 Å. Time effects are not observed with naphthalene–chloroform or *s*-trinitrobenzene–chloroform solutions.

Plots of the molar absorptivity (a_C) (Table IV) *vs.* wave length for each solvent at each temperature (not shown) displayed the typical broad bands with poorly defined maxima associated with isomeric charge-transfer systems.[10] While the changes in band shape are small, there is no doubt that these molar absorptivity curves for the 1:1 *s*-trinitrobenzene–naphthalene complex are slightly different for each solvent and that they broaden at the higher temperature. On the other hand, the formation constant is markedly sensitive to the inert solvent used (Table III). The large maximum permitted Errors in calculated values of ΔH (DEVΔH) (Table III), obtained with spectral data accurate to 1%, emphasize the importance of an error analysis based on experimental limits of error. The size of DEVΔH prevents analytical arguments based on ΔH. However, the marked variation in K-values is not reflected in the heats of formation (ΔH). The variations of K and a_C cannot be attributed to the dielectric constant (Table III), refractive index, or another electrical property of the solvent. Moreover the consistent results obtained in our analyses definitely eliminate any explanation which attributes the variations in K with solvent to the neglect of undefined nonspecific interactions in the solutions. Thus the new work does not support Mulliken's views of the role played by the solvent in charge transfer.[24] The Dewar–Lepley[26] theory of charge transfer in π-complexes is not contradicted by the new data.

While the size of terms like $K_3a_{C_3}$ in eq. 4 will not alter the preceding discussion, contact charge-transfer contributions ($K_3a_{C_3}$, $K_4a_{C_4}$. . .) in the reaction scheme A are predicted to be negligible.[11-14,38]

The variation in K and a_C in the first four solvents (Tables III and IV) and in CS_2 can be explained qualitatively if it is supposed that in *n*-hexane, *n*-heptane, and cyclohexane either the TN or LN complex is favored to a varying degree by the definitive geometry of the solvent. The lower values for K in CCl_4 could be attributed to the absence of structure in the solvent. Equations which support this view are given elsewhere.[21,39] The low value for K in $CHCl_3$ has already been attributed to complex formation between naphthalene and the solvent.

Acknowledgments.—Financial support for this work was provided by the United States Air Force under grant No. AF-AFOSR 62-19, monitored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research. C. C. T. is indebted to the National Science Foundation for the award of a Cooperative Graduate Fellowship.

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[38] S. F. Mason, *Quart. Rev.* (London), **15**, 287 (1961).

[39] P. A. D. de Maine, *J. Mississippi Acad. Sci.*, in press.

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIF.]

Equilibria in Solutions of Cyanuric Acid and its Chlorinated Derivatives[1]

BY A. P. BRADY, K. M. SANCIER, AND GLORIA SIRINE

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In addition to OH^-, H^+, ClO^-, and HClO, ten organic species are possible in aqueous solutions of cyanuric acid and its salts in the presence of Cl(+1). These are found to be in labile equilibrium, so 11 independent equilibrium constants are necessary to describe the solution at a given arbitrary pH and over-all concentration of Cy (denoting the moiety $C_3N_3O_3$) and Cl(+1). Four of these constants are reasonably well established (although only in the case of the dissociation of water is there complete agreement) and a fifth (the third dissociation constant for H_3Cy) has been estimated. The present paper describes titrometric and spectrometric measurements that allow estimation of five of the six remaining equilibrium constants, and thus a description of the species present in compositions ranging from HCl_2Cy to Cy^{-3}. The concentration of Cl_3Cy in solution in the pH and concentration range studied is so small that only a crude lower limit can be set on the sixth constant, involving $Cl_3Cy + H_2O = HCl_2Cy + HClO$.

Introduction

Cyanuric acid is a tribasic acid in which the hydrogens may successively be replaced by positive (+1) chlorine. Trichlorocyanuric (or isocyanuric) acid and the salts of mono- and dichloro derivatives are articles of commerce. In aqueous solutions there is labile equilibrium among the various chlorinated derivatives. To avoid the problem, not germane to the present paper, of whether to write the various species as derivatives of *s*-triazine triol or the corresponding keto form (which may depend upon the pH[2]), the $C_3N_3O_3$ moiety will be denoted by Cy; *i.e.*, H_2Cy denotes the unchlorinated acid, Cl_2Cy^- the anion of the dichloro derivative, etc. In aqueous solutions containing hypochlorite, in addition to the inorganic species HClO, ClO^-, H^+, and OH^-, ten organic species could conceivably be present. These are shown schematically in Fig. 1, which also serves to define most of the equilibrium constants. For clarity the equations are not balanced, and thus do not show formation of HClO or ClO^-, or changes in acidity. For setting up the K's, the reactions are considered to proceed downward and to the right; the hydrolysis of positive chlorine is considered to be through H_2O with the production of HClO in the first row to the left and through OH^- with the production of ClO^- in the remaining two.

The fourteen species that could be present require eleven independent constants to describe the system completely at a given pH and over-all concentration of positive chlorine and of cyanuric acid. Four of these, involving the dissociation constant of water, hypochlorous acid, and the first and second dissociation constants of cyanuric acid, are in the literature (although there is some disagreement concerning all except that of water) plus a crude estimate of a fifth (K_{12}) but, so far as the authors are aware, not even an estimate of any of the remaining six has appeared.

The present paper reports some titration and spectrometric studies which allow estimation of five more

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[1] Supported in part by the Procter and Gamble Co., Cincinnati, Ohio.

[2] Manuscript in preparation.

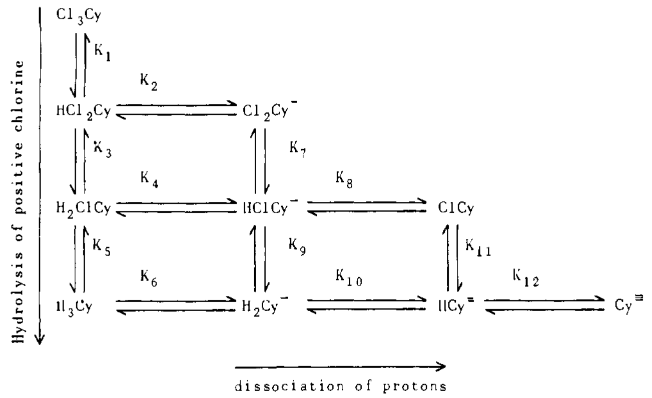

Fig. 1.—Equilibria among cyanuric acid and its chlorinated derivatives.

independent constants—or, more properly, concentration quotients referring in the main to an ionic strength of approximately 0.5, since no activity coefficients were measured. Only a lower limit could be set on the sixth, K_1.

Experimental

Materials.—Cyanuric acid (Grace Chemical Co., >98% pure) was dissolved in alkaline solution, filtered, and acidified with H_2SO_4, and the precipitate was dried at 150°. The chlorinated derivatives were prepared in these laboratories by direct chlorination of an aqueous solution of the corresponding salt. Stock solutions of sodium hypochlorite were prepared from commercial bleach (Clorox Chemical Co.) and analyzed for ClO^- by the thiosulfate–iodine method. Because of the method of manufacture, the hypochlorite solution typically contained 100 mole % Cl^-, <2 mole % ClO_3^-, and less than 10^{-3} mole % heavy metals, based on the ClO^- concentration. All buffers were prepared from analytical grade chemicals.

Procedures.—For the titration curves a Beckman Model G pH meter was used. The Model 1170 calomel electrode was used with an asbestos fiber, since electrodes with a palladium contact do not behave well in hypochlorite solutions. Absorption spectra were measured with a Cary recording spectrometer, Model 14. All determinations were at 23 ± 2°.

For the titrations, crystalline samples of the appropriate chlorinated derivative were used. For the spectral work in alkaline solutions the preferred method was to mix buffered solutions of known concentrations of cyanuric acid and sodium hypochlorite. Comparison with authentic samples in the same buffers showed that, upon mixing, equilibrium was attained in less than one second; the mixing method was preferred because of its convenience and because any possible decomposition was minimized by the rapidity of the measurements.

Results

Titration Curves.—The titration curves for H_3Cy and its three chlorinated derivatives are given in Fig. 2. That for H_3Cy is straightforward enough; a value for pK_6 of 7.0 is obtained from both the mid-point pH and the use of the whole curve by a plot of pH *vs.* log $[c_t/(c_a - c_t)]$, when c_t is the over-all concentration of the titrant at a given pH and c_a that of the acid (H^+ and OH^- can be neglected in comparison with c_a and c_t). Omitting some older results, the p*K* of H_3Cy has been reported as 6.8,[3] 6.5,[4] and 7.2.[5] For the sake of consistency and because there is no particular reason to pick any other, the value found here will be used for further calculations.

The curve for HCl_2Cy is also straightforward and gives $pK_2 = 4.0$, either from the titration curve or from the initial pH. It should be noted that the mid-point of the curve (pH 4.1) does not give pK_6 because the hydrogen ion concentration is not negligible compared with that of the acid; the p*K* is given by the pH at which $(c_t + (H^+))/(c_a - (c_t - H^+)) = 1$.

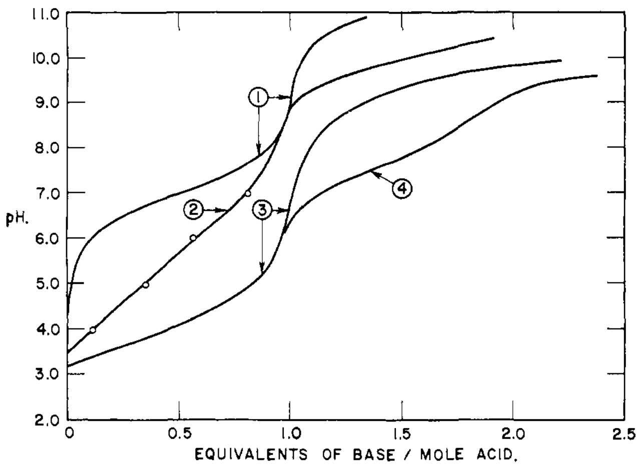

Fig. 2.—Titration curves of (1) H_3Cy, (2) H_2ClCy, (3) HCl_2Cy, and (4) Cl_3Cy; circles calculated, see text.

Up to a pH of slightly over 6, the curve for Cl_3Cy is identical within experimental error with that for HCl_2Cy. Above this pH another acid is being titrated with a pH of 7.5–7.6 (the flattening at pH ≥9 is to be expected from other processes, to be discussed below) and this is almost certainly HClO. Latimer[6] chose $pK = 7.5$ for the dissociation constant of HClO, a value experimentally confirmed by Friedman.[7] Thus little can be said about pK_1 other than to put a rather crude upper limit on it from an estimate of the precision of the titration curves of $pK_1 \leq 0.3$.

The curve for H_2ClCy requires special treatment. It can be seen that it is almost linear and must result from a mixture. Further, the mixture must be in mobile equilibrium, since the solution can be brought into an alkaline region where spectrophotometry has shown establishment of equilibrium to be fast, and the same curve can be obtained in a reverse titration with acid. Hydrolysis of HOCl and H_3Cy would give an entirely different curve from that experimentally found. The logical reaction to consider, whose concentration quotient will be denoted by $K_{13}(=K_5/K_3)$, is

$$2H_2ClCy = H_3Cy + HCl_2Cy \qquad (1)$$

Denoting by [PC] the total over-all concentration of positive chlorine and by [CA] that of the Cy moiety, the material balance equations are

$$[PC] = (H_2ClCy) + (HClCy^-) + 2HCl_2Cy + 2Cl_2Cy^- \qquad (2)$$

$$[CA] = (H_3Cy) + (H_2Cy^-) + (H_2ClCy) + (HClCy^-) + (HCl_2Cy) + (Cl_2Cy) \qquad (3)$$

since no other species are important in the pH range (<8) of interest. By noting that for the monochloro derivative [CA] = [PC], and by substituting appropriate equilibrium constants, it can be shown that

$$(H_2ClCy)/[CA] = \{2[K_{13}(1 + K_6/(H^+))]^{1/2}[1 + K_2/(H^+)]^{1/2} + [1 + K_4/(H^+)]\}^{-1} \qquad (4)$$

$$(HCl_2Cy)/[CA] = \{(H_2ClCy)/[CA]\}\{K_{13}[1 + K_6/(H^+)]/[1 + K_2/(H^+)]\}^{1/2} \qquad (5)$$

$$(H_3Cy)/[CA] = K_{13}\{(H_2ClCy)/[CA]\}^2/\{(HCl_2Cy)/[CA]\} \qquad (6)$$

Equations 4–6 allow calculation of all uncharged species, which, in turn, through a simple charge balance, determines the predicted titration at any given pH,

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(3) C. E. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 3420 (1939)

(4) R. C. Hirt and R. G. Schmitt, *Spectrochim. Acta*, **12**, 127 (1958).

(5) "The Merck Index," Merck and Co., Inc., Rahway, N. J., 1960.

(6) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(7) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

which then can be compared with the experimental result. There are two arbitrary parameters, K_{13} and K_4. This may seem to offer a wide variety of choices that will fit the experimental curve well enough, but the choices are surprisingly limited. The operational technique was to assume a value for K_4 and various values of K_{13} and then to compare the predicted titration at pH 4–7 with the actual titration, the criterion of fit being that K_{13} remains constant. Symmetry indicates that pK_4 be somewhere in the neighborhood of 5.7. At an assumed value of 5.5 or 5.9 the apparent value of pK_{13} varied widely with pH, whereas the assumptions that pK_4 = 5.7 and pK_{13} = 1.0 fit the curve reasonably well (open circles in Fig. 2), and these values will be adopted. A check on the consistency of these choices with the spectrophotometric results will be given below.

Spectrometric Results.—Hypochlorous acid has an absorption peak at about 2300 Å. with an extinction coefficient of about 100 l. mole^{-1} cm.$^{-1}$. However, the intense cyanurate absorption completely masks this peak, so direct spectrometric determination of hydrolyzed positive chlorine is not practical in acid solution. The hypochlorite ion, on the other hand, has a peak of 2910 Å. where cyanurate, whether chlorinated or not, absorbs very little.[2]

Table I summarizes the results at pH 9.7 in terms of the observed apparent molar extinction coefficients of the hypochlorite ion, ϵ, defined as the optical density divided by [PC], and a quantity z, to be defined later. This pH was chosen so that the presence of HCy^{-2} would give only a minor correction and any uncharged species could, for present purposes, be ignored. The molar extinction coefficient of the hypochlorite ion in the carbonate buffer (Table IA) was found in separate experiments to be largely independent of buffer concentration and of pH (taking into account the formation of HClO at lower pH's)—neither of these statements is true in the case of the borate buffer, so treatment of the latter results will be deferred. In the case of the carbonate buffer, Beer's law is not obeyed exactly, in that ϵ decreases from 361 l. mole^{-1} cm.$^{-1}$ at 0.00071 M to 351 at 0.00423 M, but the change with concentration is slow enough not to cause trouble in the calculations to follow. In previous work, values of ϵ of 330 to 350 were reported[7-9]; the only statement we have found concerning Beer's law is Friedman's to the effect that it is obeyed within a few per cent in the range 0.0002–0.004 M.[7]

TABLE I

SPECTROMETRIC RESULTS AT pH 9.7 AND λ 2910 Å.

Concentrations in mmoles/l.

[PC]	[CA]	ϵ, l. mole^{-1} cm.$^{-1}$	z
	A. Buffer 0.5 M $NaHCO_3$ + NaOH		
0.71	0.0	361	. .
	.48	203	1.55
	.72	152	1.76
1.41	.0	357	. .
	.71	200	1.15
	.92	164	1.24
	1.42	111	1.46
2.82	0.0	355	. .
	1.88	135	1.07
	2.82	79	1.29
4.23	0.0	351	. .
	1.41	208	0.820
	2.11	162	0.909
	2.82	117	1.00
	4.22	59	1.20
	B. Buffer 0.5 M H_3BO_3 + NaOH		
1.41	0.0	298	. .
	.71	177	1.22
4.23	.0	300	. .
	1.41	187	0.875
	2.11	141	0.938
42.3	0.0	305	. .
	14.1	137	0.605
	21.1	78	0.675

No experimental evidence was found for the presence of Cl_3Cy in these solutions; indeed, from the titration results none would be expected. For the reaction

$$Cl_3Cy + 2OH^- = Cl_2Cy^- + ClO^- + H_2O$$

$K = K_1K_2K_H/K_w^2$, where K_H and K_w are the dissociation constants of hypochlorous acid and of water. Taking $K_1 \geq 10^{-3}$, $K_2 = 10^{-4}$, $K_H = 10^{-7.5}$, and $K_w = 10^{-14}$, then $K \geq 10^{13.4}$. Thus at $(ClO^-) = (Cl_2Cy^-) = 2 \times 10^{-2}$ M (about the highest concentrations tried) and $(OH^-) = 5 \times 10^{-5}$, the concentration of Cl_3Cy is calculated to be $<5 \times 10^{-9}$ M. Thus the material balance equations appropriate to pH 9.7 are

$$[PC] = 2(Cl_2Cy^-) + (HClCy^-) + (ClCy^{-2}) + (ClO^-) \quad (7)$$

$$[CA] = (Cl_2Cy^-) + (HClCy^-) + (ClCy^{-2}) + (H_2Cy^-) + (HCy^{-2}) \quad (8)$$

Combination of eq. 7 and 8 with the equilibrium constants gives eq. 9

$$(2z - 1)(ClO^-)^2/(OH^-)^2 = -A(z - 1)(ClO^-)/(OH^-) + B \quad (9)$$

where

$$z \equiv [CA]/\{[PC] - (ClO^-)\}$$
$$A \equiv K_7(1 + K_8/(H^+))$$
$$B \equiv K_7K_9(1 \pm K_{10}/(H^+))$$

Equation 9 is formally equivalent to Bjerrum's treatment of the calculation of association constants[10] except that it takes into account other processes and is in a more convenient form for present purposes. The value of (ClO^-) can be taken as $[PC](\epsilon/\epsilon_0)$, where ϵ is the apparent extinction coefficient of the solution and ϵ_0 is the extinction coefficient of hypochlorite ion at approximately the same concentration in the same buffer. This in turn fixes z, given in the last column of Table I. The quantity z is the mean ratio of Cy to bound positive chlorine, and if it dropped below 0.5, which it does not, the presence of Cl_3Cy would have to be considered. The fact that z occasionally drops below unity immediately demands that the dichloro derivative be taken into account.

It is evident from eq. 9 that a plot of $(2z - 1)\cdot(ClO^-)^2/(OH^-)^2$ as ordinate *vs.* $(z - 1)(ClO^-)/(OH^-)$ as abscissa should give a straight line with slope $-A$ and intercept B. Such a plot is given in Fig. 3 and a least square line through the open circles gives $A = 1.40 \times 10^2$ and $B = 7.2 \times 10^2$.

Turning to the borate buffer, in Table IB, it can be seen that the extinction coefficient of the hypochlorite ion is considerably lower than in carbonate buffer. Experiments not given in the table tend to indicate that the decrease is associated with the amount of undissociated H_3BO_3 present, but such a detailed interpretation is not necessary for present purposes. All that is necessary is to note that the borate removes some of the hypochlorite from spectroscopic detection and that the buffer is in large excess, so that the relative amount removed should not depend strongly on

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[8] R. E. Corbett, W. S. Metcalf, and F. G. Soper, *J. Chem. Soc.*, 1927 (1953).

[9] M. Auber and I. Dostrovsky, *ibid.*, 1105 (1954).

[10] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

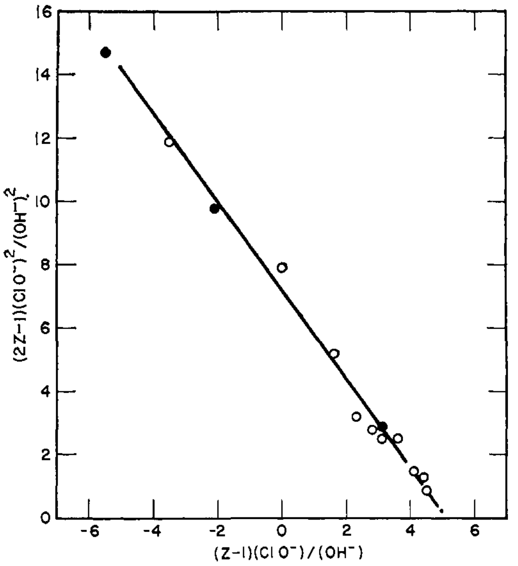

Fig. 3.—Plot of spectrometric results according to eq. 9: ○, carbonate buffer; ●, borate buffer corrected (see text).

the concentration of hypochlorite, which is borne out by the data in the table.

For computation of z, which arises from the material balance eq. 7 and 8, in the borate buffer (ClO^-) is to be interpreted as the total hypochlorite not bound to a Cy moiety and can be taken, as before, as $[\text{PC}]\cdot(\epsilon/\epsilon_0)$. The (ClO^-) terms appearing outside of z in eq. 9 arise from the use of concentration quotients and should be interpreted as free hypochlorite only, given by $[\text{PC}]/(\epsilon/{}^0_0)$, where ${}^0_0$ is the true extinction coefficient of the hypochlorite ion, which was taken as that given by the results in carbonate buffer. The two entries in Table IB at the highest concentration were a check (negative) for the possible presence of Cl_3Cy and fall far outside the range of Fig. 3; the other three, with the above interpretation of the apparent extinction coefficients, are shown in Fig. 3 as the filled circles. They fall quite satisfactorily on the line.

The next step is to untangle the constants in A and B. The present work gives no information on K_{10}; taking the literature value[4] of $\text{p}K_{10} = 10.6$, the value in parentheses in the definition of B is 1.12, to give $K_7K_9 = 5.8 \times 10^2$. Two methods will be used to estimate K_8, both of which admittedly have drawbacks: the estimation of K_2, K_4, K_6, and K_{13} from acid solutions in combination with A and K_7K_9, and the titration of H_2ClCy to pH 9.7 in combination with the values of A and B.

The following relation may readily be derived by a transformation of the definition of A

$$K_8 = (\text{H}^+)[(A/K_4)(K_2K_6K_{13}/K_7K_9)^{1/2} - 1] \qquad (10)$$

Substituting the previously derived values for the K's and $(\text{H}^+) = 2 \times 10^{-10}$ gives $\text{p}K_8 = 9.4$. This is by far the simplest and most elegant way to arrive at a value for K_8. However, it is desirable to obtain a check on the reasonableness of the value so obtained, which can be done by examination of the titration curve for H_2ClCy on the alkaline side together with Fig. 3.

The number of equivalents of base consumed by H_2ClCy at pH 9.7 was 1.345 (excluding straight dilution); the concentration at this pH, taking into account the added NaOH solution, was 5.80×10^{-3} M. The concentration of ClO^- is most expeditiously found by successive approximations: assuming a value for (ClO^-), calculating the resulting z and hence the coordinates on Fig. 3 and comparing the results with the experimental line, readjusting (ClO^-), and so on. The value of (ClO^-) so found is 0.815×10^{-3} M, which leads to an expected titration, including only conversion to uninegative species (HClCy^-, Cl_2Cy^-, ClO^-) of 1.140, thus leaving a 0.205 equivalent (corresponding to 1.19×10^{-3} M) of doubly charged species. It is not only difficult, but unjustified in view of the accuracy involved (and because of compensating error), to split this into ClCy^{-2} and HCy^{-2}. A hypothetical solution is then considered, in which doubly charged species are subtracted out, to give $[\text{CA}] = [\text{PC}] = 4.61 \times 10^{-3}$ and, as before, $(\text{ClO}^-) = 0.815 \times 10^{-3}$. A new value of $(2z - 1)(\text{ClO}^-)^2/(\text{OH}^-)^2$ and of $(z - 1)(\text{ClO}^-)/(\text{OH}^-)$ is then calculated, and, since the intercept is not dependent upon the value of z, a new A (9.4×10^2) is calculated. The ratio of the new A to the experimental A is approximately (since HCy^{-2} has been neglected) equal to $(1 + K_8/(\text{H}^+))$. The value of $\text{p}K_8$ found by this procedure is 10.0. This can hardly be called excellent agreement with the 9.4 found by the first procedure, but on the other hand is reasonably good considering the curve-fitting necessary to find K_4 and K_{13}, used in the first method, and the flatness of the titration curve and the neglect of HCy^{-2} in the second method.

If one were interested only in the second dissociation constant of H_2ClCy it would be safest to take some sort of average of the two values of the two $\text{p}K_8$'s of the above paragraph. For self-consistent calculations on the whole system, however, the value of 9.4 should be chosen and will be used. This immediately places $\text{p}K_7$ at -1.7 and $\text{p}K_9$ at -1.1.

Discussion

The constants derived in previous paragraphs, together with those derivable from the cycles indicated in Fig. 1, are summarized in Table II. It is difficult to discuss the accuracy of the results because of their interdependence, but some remarks can be made.

Table II

Self-consistent Values for pK's of Fig. 1

n	pK_n	Source	n	pK_n	Source
1	<0.3	Estd.	7	− 1.7	Titration, spectrum
2	4.0	Titration	8	9.4	Titration, spectrum
3	3.1	K_2, K_4, K_7, K_w, K_H	9	− 1.1	Titration, spectrum
4	5.7	Titration	10	10.6	Ref. 4
5	4.1	K_4, K_6, K_9, K_w, K_H	11	− 0.1	K_8, K_9, K_{10}
6	7.0	Titration	12	~13	Ref. 2

The titration curves have been repeated many times, and the precision is well within 0.1 pK unit for $\text{p}K_2$ and $\text{p}K_6$. The value for $\text{p}K_4$ required curve-fitting but, as already remarked, the fit becomes poor if $\text{p}K_4$ is varied more than ±0.1 pK unit. The quantities A and B of eq. 9 seem reasonably well established, but require knowledge of $\text{p}K_8$ and $\text{p}K_{10}$ in order to obtain $\text{p}K_7$ and $\text{p}K_9$. The influence of $\text{p}K_{10}$ is small and a reasonable error in the literature value can be neglected (except in calculating $\text{p}K_{11}$). The value for $\text{p}K_8$ is derived (eq. 10) by a combination of a number of experimental quantities and is probably the least accurate. An error in $\text{p}K_8$ introduces an error in $\text{p}K_7$ but not in a one-to-one manner. If, for example, $\text{p}K_8$ was assumed to be 10.0 instead of 9.4, $\text{p}K_7$ would be changed by 0.3 rather than 0.6 pK unit. A value for $\text{p}K_8$ of over 10 seems unlikely since one would expect the ratio K_8/K_{10} to be similar to K_4/K_6, as is the case for the values chosen. An error in $\text{p}K_7$ introduces an error in $\text{p}K_9$, in the opposite direction, in a one-to-one manner.

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