395. *Studies of* N-*Halogeno-compounds. Part IV.* The Reaction between Ammonia and Chlorine in Aqueous Solution, and the Hydrolysis Constants of Chloroamines.*

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The reaction between ammonia and chlorine or hypochlorous acid in dilute aqueous solution has been examined spectrophotometrically. The product in solutions of pH < 3 is nitrogen trichloride, of pH 3—5 dichloroamine, and of pH > 8 monochloroamine. In strongly alkaline solution, chloroamine is hydrolysed to hypochlorite ions.

THE reaction between chlorine and ammonia in aqueous solution has been examined by a distribution method by Chapin (*J. Amer. Chem. Soc.*, 1929, **51**, 2113); above pH 4·4 dichloroamine was formed and below pH 4·4 nitrogen trichloride, the change in product occurring sharply at this pH. Above pH 8·5 only monochloroamine was obtained. Chapin also identified the dichloroamine by analysis. The results of the spectroscopic examination of solutions much more dilute than those used by Chapin are in substantial agreement with these conclusions. Above pH 8, the absorption spectra show a mixture of chloroamine and hypochlorite, from 5 to 8 a mixture of mono- and di-chloroamine, and below pH 3 only nitrogen trichloride.

The absorption spectra of these unstable solutions were measured by the flow method described in a previous paper (Metcalf, *J.*, 1942, 148). In the Figure are plotted the ultra-violet absorption spectra of hypochlorite ions and chloroamine. Those of dichloroamine and nitrogen trichloride have been published previously (*loc. cit.*). At any one pH only two absorbing substances are present, so that the points of intersection of the curves are isosbestic points (cf. Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103), and the curves for equilibrium mixtures pass through them. As the total concentration of hypochlorous acid liberated on hydrolysis is known, the proportion of it present as hypochlorite, chloroamine, dichloroamine, or nitrogen trichloride can be calculated from the extinction curve of the equilibrium mixture.

Whilst the equilibrium between chloroamine and hypochlorite is immediately attained and the solutions are relatively stable, the equilibria between chloroamine and dichloroamine, and between dichloroamine and nitrogen trichloride are approached but slowly. Moreover, solutions that contain dichloroamine are very unstable (Table 2) and cannot be left for any length of time to attain equilibrium. It has therefore only been possible to determine the equilibrium constant of the first of the following reactions:

$$NH_2Cl + OH^- \rightleftharpoons NH_3 + OCl^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$H^+ + 2NH_2Cl \rightleftharpoons NHCl_2 + NH_4^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$H^+ + 3NHCl_2 \rightleftharpoons 2NCl_3 + NH_4^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The Hypochlorite–Chloroamine Equilibrium.—The equilibrium $4H^+ + 3Cl^- + NCl_3 \rightleftharpoons NH_4^+ + 3Cl_2$, which might perhaps be expected in sufficiently acid solutions, could not be detected in concentrated hydrochloric acid. In the equilibrium, $NH_2Cl + OH^- \rightleftharpoons NH_3 + OCl^-$, the total active chlorine is estimated by iodometric titration and the amount of it present as hypochlorite and chloroamine is deduced from the extinction at 3100 Å (see Figure). The hydroxyl-ion concentration is taken as the concentration of the sodium hydroxide present. The total ammonia added is known, and the concentration of ammonia in the solution is obtained by subtracting the concentration of chloroamine from it. Thus all the concentration terms (in moles per litre) in the expression $[NH_3][OCl^-]/[NH_2Cl^-][OH^-] = K'$ are known. The values of K' for various concentrations of sodium hydroxide, ammonia and active chlorine are given in Table 1.

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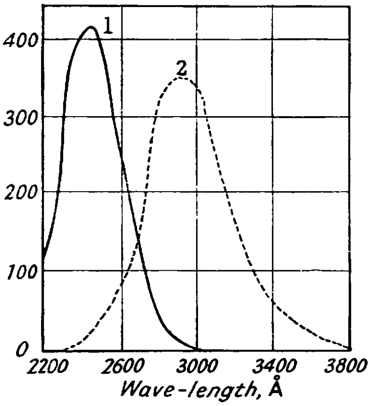
* Previous papers that form a part of this series are those by Mauger and Soper, *J.*, 1946, 71; Edmond and Soper, *J.*, 1949, 2942; and Hurst and Soper, *J.*, 1949, 107.

The effect of displacing the equilibrium by decreasing the ammonia concentration from 0·01M to 0·002M while keeping the other concentrations constant is shown in Table 1*A*. Table 1*B* shows the effect of increasing the hydroxyl-ion concentration from 0·5M to 2·5M, and Table 1*C* illustrates the effect of varying the concentration of ammonia. In the last series the possible percentage error is greater than in 1*A* or 1*B*; since, of the various equilibrium concentrations that of the hypochlorite ion is measured directly with an estimated error of ±2%. This introduces similar errors in the deduced concentrations of NH_2Cl(= [total active Cl] − [OCl^-]) and of NH_3(= [total NH_3] − [NH_2Cl]) except in series *C* where the difference (total [NH_3] − [NH_2Cl]) is smaller and the percentage error larger. The overall mean value of K' is $1{\cdot}6 \times 10^{-3}$.

K' is related to the hydrolysis constant k_h of the hydrolysis of monochloroamine, $NH_2Cl + H_2O \rightleftarrows NH_3 + HOCl$, by the equation $K_h = K'K_w/K_a$, where K_w is the ionic product for water and K_a is the acid ionisation constant of hypochlorous acid.



1. *Chloroamine.*
2. *Hypochlorite ion.*

If the activity coefficient of neutral molecules is unity and those of univalent ions are equal at a given ionic strength, then K' and K_h are approximately independent of ionic strength and unchanged by the substitution of activities for concentrations.

TABLE 1.

		Active Cl,					Active Cl,		
[NaOH], M	[Total NH_3], M	as [HOCl], 10^{-3}M	as OCl′, %	$10^3K'$ (15°)	[NaOH], M	[Total NH_3], M	as [HOCl], 10^{-3}M	as OCl′, %	$10^3K'$ (15°)
				A					
0·5	0·010	2·72	10·0	1·67	0·5	0·0020	2·20	51·0	1·90
0·5	0·0060	2·48	17·4	1·66	1·0	0·0020	2·46	65·0	2·10
				B					
0·5	0·010	2·43	8·45	1·52	0·7	0·010	3·20	12·9	1·52
2·5	0·010	2·64	31·0	1·55	0·8	0·010	3·06	15·1	1·64
0·5	0·010	3·23	10·0	1·57	0·9	0·010	3·04	15·5	1·51
0·6	0·010	2·31	9·9	1·70					
				C					
0·8	0·010	5·04	18·3	1·63	0·8	0·0060	3·70	22·6	1·23
0·8	0·0090	5·12	17·5	1·27	0·8	0·0050	3·72	32·5	1·62
0·8	0·0080	4·40	23·0	1·77	0·8	0·0040	3·28	42·4	1·95
0·8	0·0070	4·45	25·0	1·47					

The value of K_w being taken as $4{\cdot}7 \times 10^{-15}$ (" International Critical Tables ") and that of K_a as $2{\cdot}7 \times 10^{-8}$ (Ingham and Morrison, *J.*, 1933, 1200), the value of the hydrolysis constant K_h is $2{\cdot}8 \times 10^{-10}$ at 15°.

The Monochloroamine–Dichloroamine Equilibrium.—The rapid decomposition of dichloroamine does not permit a test of the constancy of this equilibrium over a period of time, although changes in the spectra were much slower after 3 hours. The displacement of the equilibrium with increasing acidity is due to the removal of free ammonia as NH_4^+, equation (2) giving the overall reaction. Absorption curves of the solution with 10^{-3}M-hypochlorous acid and 5 × 10^{-3}M-ammonia buffered with phosphate showed an instantaneous disappearance of hypochlorite ion and the presence of monochloroamine and dichloroamine over the pH range 5—8. We do not consider estimates of the relative amounts present in this unstable solution satisfactory for the evaluation of the equilibrium constant involving dichloroamine. Below pH 3, with ammonia solution from 5 × 10^{-3}M to 1·5 × 10^{-1}M and hypochlorous acid from 2·25 to 4 × 10^{-3}M, only nitrogen trichloride is present.

Equilibria involving nitrogen trichloride are approached slowly. A solution of hypochlorous acid and ammonia in N/10-hydrochloric or N/10-acetic acid contained one third of the active chlorine as nitrogen trichloride, immediately after being mixed. After 1 hour, two thirds was present as the trichloride, and after 2 and 3 hours no dichloroamine remained. This disappearance of dichloroamine from solutions more acid than pH 3 may be due to the relative instability of dichloroamine.

Table 2 shows that solutions which have been proved spectroscopically to contain dichloroamine are much the most unstable, there being a minimum instability of mixtures of ammonia and hypochlorous acid in the pH range 4—5.

TABLE 2.

pH	2·8	3·0	3·9	4·4	6·3—9·2
Time of half decomp. at 15°	10 hr.	7 hr.	10 min.	20 min.	>3 hr.

Solutions of nitrogen trichloride in water are stabilised by small amounts of acid, and those of chloroamine by small amounts of alkali, such as a slight excess of ammonia. Anhydrous solutions of both nitrogen trichloride and of chloroamine in organic solvents are comparatively stable in the absence of light. These facts suggest that the slow decomposition of both compounds in water may perhaps involve the intermediate formation of the unstable dichloroamine as a first step.

None of the spectra of solutions described in this paper was noticeably affected by addition of M/10-sodium chloride, or by use of chlorine water in place of pure hypochlorous acid.

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