[CONTRIBUTION FROM THE BIOCHEMIC DIVISION, BUREAU OF ANIMAL INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

THE INFLUENCE OF *P*H UPON THE FORMATION AND DECOMPOSITION OF THE CHLORO DERIVATIVES OF AMMONIA

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The Chloro-amines under Decreased *P*H.—The writer[1] demonstrated that in aqueous solution maximum purity is reached by monochloro-amine (NH_2Cl) above *P*H 8.5 and by dichloro-amine ($NHCl_2$) at *P*H 4.5–5.0. In Fig. 1 are shown percentage recoveries of available chlorine from such solutions of the chloro-amines, containing an excess of ammonium ion, subjected to decreased *P*H. Each atom of constituent chlorine in all three chloro derivatives (including nitrogen trichloride), as in hypochlorite, liberates two atoms of available chlorine under the methods of assay employed.[2] Evidently the *P*H ranges of maximum stability coincide with the ranges of maximum purity. Under current hypotheses[3] the curves of Fig. 1 would be explained through the operation of pairs of competing reactions, *e. g.*, $2NH_2Cl + HCl \longrightarrow NH_4Cl + NHCl_2$ and $3NH_2Cl \longrightarrow NH_4Cl + N_2 + 2HCl$, catalyzed by acid. But each of these reactions may be complex; the second, in particular, inasmuch as it is also catalyzed by alkali,[4] leaves the mechanism obscure.

The action of excess hypochlorite upon ammonium ion is known to progress to the formation of nitrogen trichloride. Stoppage of the chlorination at the stage of either chloro-amine demands, first, a limited proportion of the chlorinating agent, and, second, a sufficiently high *P*H. Supplementing these established facts, the writer finds two fundamental general hypotheses adequate to account for the various products and decompositions which result from the chlorination of ammonium ion over a wide range of conditions: Hypothesis I. Under the influence of hydrogen ion, all three chloro derivatives of ammonia yield ammonium ion and hypochlorous acid. Hypothesis II. Under the influence of hydroxyl ion, all three chloro derivatives of ammonia yield chloride ion, the consequent oxidation of the residual atoms leading to a variety of associated products.

The first hypothesis was implied by Marckwald and Wille[4] in accounting for the production of nitrogen trichloride from acidified monochloro-amine, data regarding dichloro-amine not being in their possession. The

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[1] R. M. Chapin, THIS JOURNAL, 51, 2112 (1929).

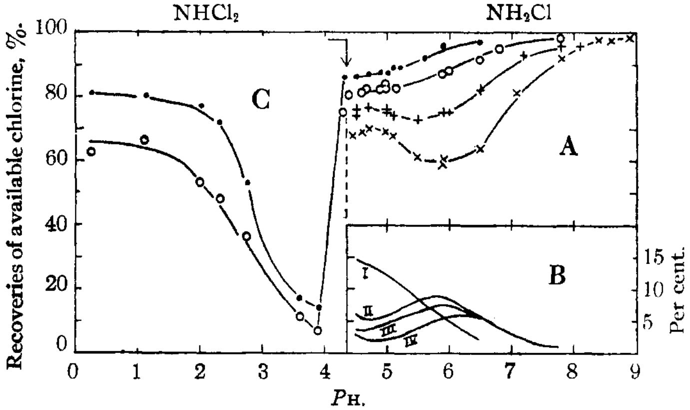
[2] Preparative and analytical methods are described under the section on Experimental Technique.

[3] M. Bodenstein, *Z. physik. Chem.*, Abt. A, 137, 131 (1928).

[4] W. Marckwald and M. Wille, *Ber.*, 56, 1319 (1923).

second is deduced from the apparently invariable presence of chloride ion among the decomposition products of all the chloro derivatives. The associated products include hypochlorite ion, nitrogen, nitrous oxide, nitrite and nitrate, which all have been identified by previous investigators.[5] Hitherto, however, practically nothing seems to have been available in the way of a quantitative study covering the alkaline decompositions of the chloro derivatives as a class.

Under Hypothesis I the formation of dichloro-amine through the acidification of monochloro-amine involves two steps: (A) $NH_2Cl + H^+ + H_2O \longrightarrow NH_4^+ + HClO$, and (B) $NH_2Cl + HClO \longrightarrow NHCl_2 + H_2O$.[6] The acidification of dichloro-amine to below *P*H 4.4 similarly yields nitrogen trichloride. Inasmuch as no loss of available chlorine is indicated in these reactions, further discussion of Fig. 1 will follow a study of the influence of increased *P*H upon the individual chloro derivatives.



●, 0.5 hour; ○, 1 hour; +, 2 hours; ×, 4 hours.

Fig. 1.—Recoveries of available chlorine at 25° from solutions of (A) NH_2Cl (0.01 *N*) and of (C) $NHCl_2$ (0.016 – 0.022 *N*) subjected to decreased *P*H. Fig. 1-B.—Rate loss per 0.5 hour; from 1-A.

$NHCl_2$ and NCl_3 under Increased *P*H.—In Fig. 2-A are shown percentage recoveries of available chlorine from solutions of dichloro-amine, containing excess ammonium ion, subjected to increased *P*H. The residual substance above *P*H 9.0 was identified as monochloro-amine through its partition ratio, C_{CHCl_3}/C_{Aq}.[1] It was concluded that the principal reaction was (C) $2NHCl_2 + 4OH^- \longrightarrow 3Cl^- + ClO^- + 3H_2O + N_2$, under which 25% of the original available chlorine should be

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[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, 1928.

[6] Discussion of the electronic mechanism of chlorination being beyond the scope of this paper, the term hypochlorous acid (HClO) is here of comprehensive significance, without regard to possible ionization.

recoverable. But during one hour at *P*H 9.6 oxy acids of nitrogen were developed equivalent to 3.0 p. p. m. of nitrogen, of which nitrite afforded 1.8 p. p. m. of nitrogen. These quantities are equivalent to 8.2% of the original available chlorine and therefore quantitatively account for the deficient recovery shown. Though the liberated ClO ion would rapidly react with excess ammonium ion present to produce monochloro-amine, there is experimental evidence for its evanescent existence. Thymol blue[7] is rather resistant toward both chloro-amines, but when a solution of dichloro-amine is treated with ammonia and thymol blue simultaneously, or in rapid succession, the color quickly fades after a transitory stage of abnormally bright blue.

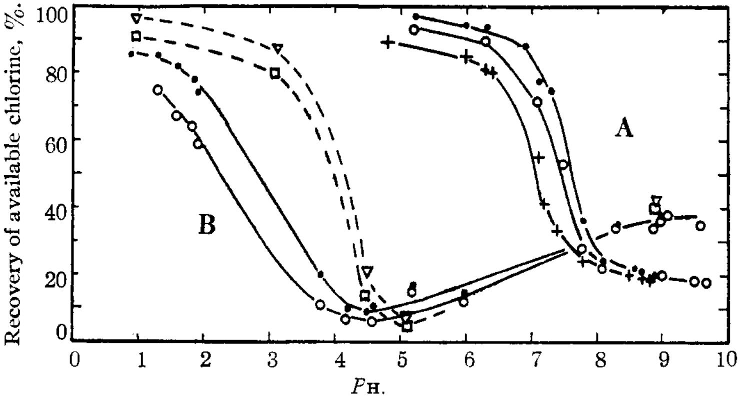

Fig. 2-B.—Nitrogen trichloride. Fig. 2-A.—Dichloro-amine.
At 25°: ●, 0.5 hour; ○, 1 hour; +, 2 hours. At 7°: ▽, 0.05 hour; ⊡, 1 hour.

Fig. 2.—Recoveries of available chlorine from solutions of $NHCl_2$ (0.01 *N*) and of NCl_3 (0.013 – 0.018 *N*) subjected to increased *P*H.

Similar experiments on nitrogen trichloride subjected to increased *P*H in the presence of ammonium ion are covered by Fig. 2-B, and monochloro-amine was similarly found to be residual at *P*H 9.6, together with a small proportion of nitrite. It was concluded that the principal reaction at that *P*H was (D) $2NCl_3 + 6OH^- \longrightarrow 3Cl^- + 3ClO^- + 3H_2O + N_2$, under which 50% of the original available chlorine should be recoverable. Failure to attain more than 40% recovery was attributed to rapid decomposition while the preparations were passing through the intermediate *P*H range during the process of mixing the alkaline buffer with the original solution.

Comparison of Figs. 1 and 2 indicates that the effect of hydroxyl ion

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[7] Indigo carmine, employed by F. Raschig, *Chem.-Ztg.*, 31, 926 (1907), for the detection of hypochlorite in the presence of monochloro-amine is much less sensitive than either thymol blue or methyl orange,

is adequate to account for the curves shown in Fig. 1. When dichloro-amine is acidified (Fig. 1-C), the loss is not due to direct action of hydrogen ion upon that substance, but to the action of hydroxyl ion upon the resulting nitrogen trichloride. When monochloro-amine is acidified (Figs. 1-A and 1-B) the free liberation of hypochlorous acid under Equation A carries some molecules of chloro-amine through to nitrogen trichloride; consequently the curves represent combined decompositions of both nitrogen trichloride and dichloro-amine under the influence of hydroxyl ion.

In view of the work of Marckwald and Wille, decompositions of monochloro-amine were not studied.

Reason arose for doubting the apparently uncontradicted statement of Anderson[8] that the passage of chlorine into excess aqueous ammonia of varied concentration always affords a considerable proportion of oxygen at all stages. He reported 13.8% in the dried gas evolved from "strongest" ammonia water, but unfortunately gave neither his method of preparation of chlorine nor a test for its purity, nor assurance that the evolved gases were freed from ammonia. Here the chlorine was prepared from hydrochloric acid and specially made manganese dioxide, and showed only a trace insoluble in sodium hydroxide solution. About 75 cc. of the gases evolved from the chlorination of excess ammonia water, after standing for about one hour, was drawn into a gas buret. The confining liquid was normal sulfuric acid tinted with methyl orange. Thorough shaking in the buret left the pink unchanged, insuring absence of both ammonia and chloro derivatives from the gas measured. The absorbing agent for oxygen was alkaline pyrogallol, and the fitness of the absorption pipet was proved through a final assay of outdoor air. "Ammonium hydroxide, C. P., sp. gr. 0.90" was chlorinated at full, half, and quarter strengths, but in each case the gas lost less than 0.2% in the pyrogallol pipet, a proportion within the limits of error of the work. The residue from the evaporation of the ammoniacal liquid afforded a distinct diphenylamine test for nitrate in the run with quarter strength, but none in the run with full strength ammonia water.

Effects of Excess Chlorine.—In Fig. 3 are shown moles of available chlorine lost per mole of ammonium when similarly buffered solutions of known concentrations were mixed. At *P*H 9 the mixtures evidently ran through rapid alternate formations of chloro derivatives and decompositions of the latter under the influence of hydroxyl ion, until either ammonium ion or hypochlorite was exhausted and only monochloro-amine and ammonium ion, or hypochlorite, remained, action being found already practically complete in one-quarter hour. Excess hypochlorite was detected after half an hour by the thymol blue test in the

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[8] Alfred Anderson, *Chem. News*, **5**, 246 (1862).

mixture of mole ratio 1.7 but not in that of ratio 1.6. At *P*H 5 the mixtures ran through a similar series of decompositions up to a mole ratio of close to 1.7, but here excess of chlorine evidently inhibited the decomposition of nitrogen trichloride under the influence of hydroxyl ion. A mixture of mole ratio 3.45 lost only 57% of its potentially ammoniacal nitrogen in half an hour, as shown by concordant determinations after reduction with As_2O_3–HCl and with sulfurous acid.

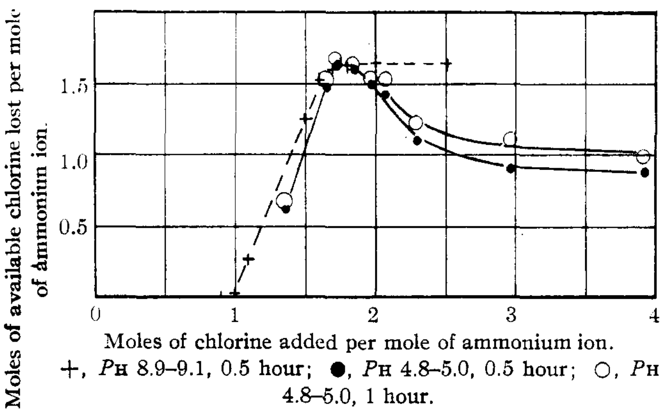

Fig. 3.—Moles of available chlorine (Cl_2) lost per mole ammonium ion (0.005 *M*) after admixture at *P*H 9.0 and at *P*H 4.9, at 25°.

When, however, the reaction was effected in much higher concentration at *P*H 5 by letting a heavily buffered ammonium solution flow[9] into a gas buret charged at atmospheric pressure with pure dry chlorine, the mole ratio 1.5 was found to leave a trace of chlorine in excess. Accordingly, departure from the relation (E), $2NH_3 + 3Cl_2 \longrightarrow 6HCl + N_2$, appears to increase with dilution. In the dilute solutions at both *P*H 5 and *P*H 9, about 40% of the departure from the mole ratio 1.5 was accounted for by the formation of nitrate. Only questionable traces of chlorate or perchlorate were detected, so search was made for nitrous oxide.[10] Preparations of 500 cc., containing the equivalent of 0.005 *M* ammonium chloride, were made by letting solutions of sodium hypochlorite, acetic acid or boric acid, and buffered ammonium chloride, flow successively into a previously evacuated flask. After one hour the gases were pumped from the warmed flask into a mercury buret, washed successively with 1 to 2 cc. of strong sulfuric acid and potash over mercury in pipets, and measured over a little distilled water. Next they were run into an ordinary pipet filled with air-saturated distilled water, and the detached pipet was shaken for five minutes. After measurement, absorption was repeated with fresh

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[9] C. T. Dowell and W. C. Bray, This Journal, 39, 896 (1917).

[10] Lord Rayleigh, *Proc. Roy. Soc.* (London), **64**, 95 (1898).

water, which took out about one-tenth as much as the first treatment. A third treatment showed no significant change. At mole ratio 1.67, which by tests with methyl orange was sufficient to leave a trace of hypochlorite, two preparations at *P*H 5 afforded equivalents of 5.2 and 6.9 cc. of water-soluble dry gas at 0° and 760 mm., which quantities, reckoned as nitrous oxide, quantitatively account for the remainder of the available chlorine consumed. But at *P*H 9 no nitrous oxide was found at mole ratios 1.60 or 1.67, so that under conditions representing the storage of nitrogen trichloride at *P*H 9 there remains a quantitative deficit.

The formation of the oxy compounds of nitrogen noted above resembles the various decompositions[5] of hyponitrous acid, $H_2N_2O_2$. Accordingly, the following mechanism is suggested. First, the production of chlorohydroxylamines, NHClOH and NCl_2OH, by metathesis, as in Equation (F), $NCl_3 + OH^- \longrightarrow Cl^- + NCl_2OH$; second, the removal of chlorine and hydrogen chloride from these by further action of hydroxyl ion, leaving the nitroyl group, HNO, which finally affords the characteristic decomposition products. Kolotoff[11] found that sodium hypobromite oxidizes hydroxylamine to hyponitrite.

Equilibria of Nitrogen Trichloride.—In Fig. 4 are shown values for the partition ratio, $C_{CCl_4}/C_{Aq.}$, of the available chlorine in solutions of varying *P*H and containing excess ammonium ion, after being held for two hours at 25°. In the one series ammonium chloride was used and hydrochloric acid, with or without potassium chloride, was the acidifying agent below *P*H 1.8; in the other, ammonium sulfate, sulfuric acid and potassium sulfate were used instead. The HI–$Na_2S_2O_3$ method of assay was employed because of its superior delicacy. Evidently the points A and A′ mark maximum purity of the resultant nitrogen trichloride. Incomplete reaction, or reversion to ammonium chloride, begins to appear in hydrochloric acid solutions a little stronger than normal and is nearly complete at 4 *N*, but none is indicated in sulfuric acid solutions up to 7 *N*, so that it cannot be due solely to low *P*H. The explanation of reversion given by Seliwanow[12] appears adequate. In aqueous solution nitrogen trichloride is in equilibrium with hypochlorous acid; (G), $NCl_3 + H^+ + 3H_2O \rightleftarrows NH_4^+ + 3HClO$. In the presence of only sulfuric acid, even of high concentration, the small concentration of hypochlorous acid necessary to stabilize nitrogen trichloride is itself stable, so that reversion is scarcely perceptible; but in presence of sufficient hydrochloric acid the reaction (H), $HClO + Cl^- \rightleftarrows OH^- + Cl_2$ may so reduce the actual concentration of hypochlorous acid that reaction (G) progresses toward the right to practical completion. It directly follows that chlorine itself is inert toward ammonium ion, chlorination occurring only when the concentration

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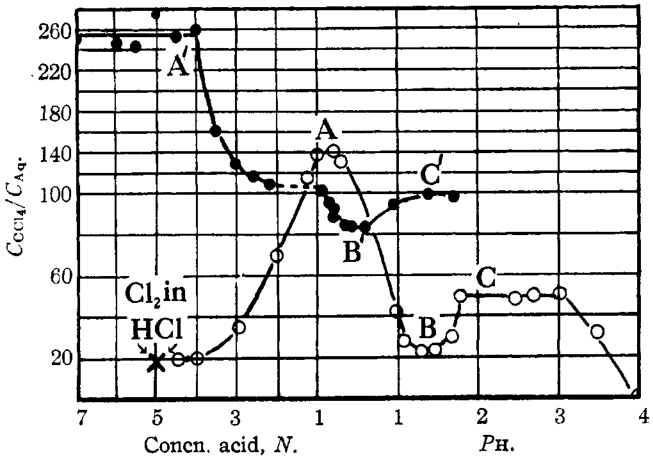
[11] S. S. Kolotoff, *J. Russ. Phys.-Chem. Soc.*, **23**, 3 (1890), through Mellor, Ref. 5.

[12] T. Seliwanow, *Ber.*, **27**, 1012 (1894).

of chloride ion is sufficiently low and the *P*H is sufficiently high to permit formation of the necessary concentration of hypochlorous acid.

In opposition to the foregoing, Noyes[13] suggests that the formation of all three chloro derivatives involves direct addition of either chlorine or hypochlorous acid, not to ammonium ion, but to ammonia, according to the scheme $NH_3 + Cl^+Cl^- \longrightarrow NH_3Cl^+Cl^- \longrightarrow NH_2Cl + H^+Cl^-$. Similarly, dichloro-amine would be derived from monochloro-amine, and finally nitrogen trichloride from dichloro-amine; but this scheme appears workable only in presence of free chlorine or hypochlorous acid. The writer does not see how the production of dichloro-amine and nitrogen trichloride from monochloro-amine through mere decrease of *P*H may be accounted for without violating Noyes' fundamental assumption that each chlorine atom retains its electronic configuration, its positive or negative character, unchanged throughout. Again, Noyes accounts for the effect of strong hydrochloric acid upon nitrogen trichloride by reversing the scheme of formation, thus, $NCl_3H^+Cl^- \longrightarrow NHCl_2 + Cl^+Cl^-$, until, after a similar passage through monochloro-amine, ammonium chloride is finally reached; but these chloro amines, and still more the corresponding chloro-ammonium chlorides, should be so comparatively little soluble in organic solvents that their presence in hydrochloric acid solutions somewhat stronger than *N* should be apparent from the partition data of Fig. 4. Lastly, the theory demands the existence of a significant concentration of ammonia in sulfuric acid solution as strong as 7 *N*. Altogether,



●, in sulfuric acid; ○, in hydrochloric acid.

Fig. 4.—Partition ratios, $C_{CCl_4}/C_{Aq.}$, of available chlorine in stored aqueous solutions of nitrogen trichloride. Initial chlorine, about 0.02 *N*.

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[13] W. A. Noyes, This Journal, 42, 2173 (1920).

the theory of Noyes appears to gain no support from the present experiments.

Returning to the discussion of Fig. 4, when the *P*H rises from the points A and A′, the decreasing partition ratios indicate formation of another substance, but complete analyses of chloroform extracts from several preparations over the range A to C showed only nitrogen trichloride. The substance in question rather persistently resisted repeated extraction by carbon tetrachloride and traces of it powerfully bleached methyl orange. It was assumed to be simply hypochlorous acid, for Hypotheses I and II applied to Figs. 1 and 2 indicate a considerable range below *P*H 4.4 over which both the action of hydrogen ion upon dichloro-amine and the action of hydroxyl ion upon nitrogen trichloride should coöperate to maintain a relatively high concentration of hypochlorous acid.

The distinct dips in the curves at the points B and B′ may perhaps be due to the presence of Cl_2O derived from the equilibrium (I) $2HClO \rightleftarrows H_2O + Cl_2O$, recently studied by Roth.[14] He found for Cl_2O the partition ratio $C_{CCl_4}/C_{H_2O} = 2.22$.

Experimental Technique

The buffers were various mixtures of phosphates (acid, middle and alkaline ranges), acetates and borates. The *P*H indicators were those recommended by Clark,[15] except that methyl orange replaced brom phenol blue, while cresol red (acid range)[16] was employed below the acid range of thymol blue. Nitrogen trichloride, when present, was extracted by carbon tetrachloride before the determination of *P*H, and, when necessary, residual bleaching powder was removed by adding to the test in the tube, before the indicator, one drop of potassium iodide solution, followed by 0.1 *N* sodium thiosulfate to decolorization. All *P*H results reported are those determined at the end of the various processes, and were, in most cases, slightly below the calculated initial *P*H.

The three chloro derivatives were prepared by rapid admixture of solutions of chlorine or hypochlorite and of ammonium ion, both buffered alike, the former, where practicable, being poured into the latter. Typical formulas were as follows: for monochloro-amine, (a) 15 cc. of 5% ammonium chloride solution, 50 cc. of 0.1 *M* sodium tetraborate, diluted to 100 cc., and (b) sodium tetraborate the same, 40 cc. of strong chlorine-water, diluted to 100 cc.; for dichloro-amine, (a) 20 cc. of 5% ammonium chloride solution, 32 cc. of 0.5 *M* sodium acetate, 8 cc. of 0.5 *M* acetic acid, diluted to 100 cc., and (b) sodium acetate and acetic acid the same, 60 cc. of chlorine-water; for nitrogen trichloride, (a) 20 cc. of 5% ammonium chloride solution, 5 cc. of 0.5 *M* hydrochloric acid, and (b) 25 cc. of chlorine-water, 20 cc. 0.5 *M* hydrochloric acid, diluted to 100 cc. The minimum periods of storage before use and the final *P*H were as follows: monochloro-amine, one hour, *P*H 9.0; dichloro-amine, two hours, *P*H 4.6–5.0; nitrogen trichloride, half an hour, *P*H 0.9.

For making changes of *P*H, sufficient solution of the chloro derivative was placed in a glass-stoppered, graduated cylinder in a water-bath, a sample for assay was pipetted out, then the remainder was immediately treated with the necessary acid or alkaline solution.

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[14] W. A. Roth, *Z. Physik. Chem.*, **145**, 289 (1929).

[15] W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 2d ed., 1922.

[16] F. R. McCrumb and W. R. Kenny, THIS JOURNAL, **51**, 1458 (1929).

Available chlorine in the two chloro-amines is determinable by the acid–iodide–thiosulfate method,[1] but in the presence of nitrite only sufficient acetic acid should be used to reach about *P*H 4. Dowell and Bray[9] reported neither iodide nor arsenious oxide as satisfactory for use in assaying nitrogen trichloride. Here it was found that about 80% of the total available chlorine of nitrogen trichloride was recoverable through a moderately acid solution of potassium iodide–hydrochloric acid from both aqueous and carbon tetrachloride solutions, and the method was employed in the presence of nitrogen trichloride in the single case of the work covered by Fig. 4. But arsenious oxide was found entirely reliable for all three chloro derivatives provided sufficient hydrochloric acid was present to effect reversion to ammonium chloride and chlorine before direct action upon arsenic trioxide occurred. A final concentration of not less than 20 volumes of the concentrated reagent per 100 of the final mixture appeared sufficient. Excess arsenic trioxide was titrated either by the bromate or the iodate method, depending upon whether the sample was in aqueous or organic solution. Solutions of pure nitrogen trichloride in chloroform afforded results closely in accord with determinations of ammonium and chloride ions made after reduction with aqueous sulfur dioxide.

The total nitrogen converted to oxy acids was determined by Nesslerization after reduction with aluminum.[17] Both sample and blank were first freed from active chlorine by the same proportions of identical solutions of potassium iodide and sodium thiosulfate, then to the blank was added acid or alkaline buffer corresponding to that already added to the sample. Just before the distillation of ammonia, each was treated with an alkaline lead solution to retain hydrogen sulfide arising from the reduction of thio acids. Nitrite nitrogen was determined colorimetrically by the A. P. H. A. method. Active chlorine was first removed by an aqueous solution of arsenic trioxide, after which the blank received the acid or alkaline buffer necessary to bring it into correspondence with the sample. The determinations noted under Fig. 3 were conducted similarly, the solution of ammonium ion there taking the place of the "buffer" referred to above.

Summary

Quantitative experiments lead to the following conclusions:

1. Elementary chlorine is inert toward ammonium ion, requiring conversion to hypochlorous acid before attack occurs.
2. Hydrogen ion induces formation of ammonium ion from each chloro-amine, particularly below a characteristic *P*H, the resulting hypochlorous acid then reacting to produce a more highly chlorinated derivative.
3. Hydroxyl ion induces formation of chloride ion from nitrogen trichloride or dichloro-amine, particularly above a characteristic *P*H, with gaseous nitrogen and hypochlorite ion as the principal associated products. With increasing dilution nitrous oxide, nitrite and nitrate also appear. To account for these oxy derivatives it is suggested that hydroxyl ion may first react by metathesis to produce chloro-hydroxylamines, which then decompose to afford the nitroyl group, characteristic of hyponitrous acid.
4. The statement that some gaseous oxygen is formed by passage of gaseous chlorine into ammonia water is apparently erroneous.

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[17] "A. P. H. A. Standard Methods of Water Analysis," 3d ed., 1917.