[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

EXPERIMENTS WITH NITROGEN TRICHLORIDE.[1]

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The experiments described in this paper were undertaken in order to study the reaction of dilute solutions of nitrogen trichloride with various substances, and especially with reducing agents.

The Preparation and Storing of Nitrogen Trichloride.—The nitrogen trichloride was prepared by the method of W. Hentschel,[2] which consists in generating it by means of the reaction

$$NH_4Cl + 3HClO = NCl_3 + HCl + 3H_2O$$

and extracting it from the aqueous solution by means of a suitable solvent. A mixture of bleaching powder and water was treated with enough hydrochloric acid to convert a large part of the hypochlorite into hypochlorous acid; and was then shaken with carbon tetrachloride in order to guard against the presence of free chlorine, which formed when too much hydrochloric acid was added. The solution was then mixed with a concentrated solution of ammonium chloride in the presence of carbon tetrachloride, and the mixture was shaken in the dark. The carbon tetrachloride was withdrawn by means of a separatory funnel and stored in a bottle which had been painted black. The bottle was fitted with an automatic buret of the Squibbs type.[3] By this arrangement the solution could be forced from the bottle by means of a pump, and the loss of NCl_3 by evaporation avoided as far as possible. The stock solutions were usually about 0.1 molal with respect to NCl_3. Hentschel used benzene as solvent in nearly all his experiments but states that hexachlorobenzene is rapidly formed when the solution is exposed to sunlight. Accordingly, we preferred to use carbon tetrachloride, since there is no possibility of a reaction between nitrogen trichloride and this solvent.[4]

In the course of the experiments it was found that in general a small quantity of free chlorine was present with the nitrogen trichloride in the CCl_4 solution. This made it impossible to determine the NCl_3 content of the solution by the method employed by Bineau[5] and others, of treating the nitrogen trichloride with a reducing agent and determining the amount of chloride in the resulting solution. The analytical methods used by us are described later in the paper.

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[1] The work described in this article and the following one was begun in the summer of 1913 at the University of California, continued there for a year, and completed by Mr. Dowell at the University of Texas.

[2] W. Hentschel, *Ber.*, 30, 2642 (1897).

[3] Eimer and Amend, Catalogue, 1913, p. 82.

[4] Cf. Chapman and Vodden, *J. Chem. Soc.*, 95, 141 (1909).

[5] Bineau, *Ann. chim. phys.*, [3] 15, 71 (1845).

In the freshly prepared solution the ratio of Cl to N was practically equal to, or a little greater than, 3 atoms of Cl to 1 of N. In only one instance was a smaller ratio found, *viz.*, 2.91 : 1; and it is probable that this was due to an error in the analysis, since the results of Hentschel,[1] Noyes and Lyon,[2] and especially Chapman and Vodden[3] seem to prove conclusively that a compound containing a smaller proportion of chlorine, as NH_2Cl,[4] cannot be obtained in appreciable amount in the presence of acid and excess ammonium chloride. The earlier results of Gattermann[5] have thus not been confirmed.

The stock solutions of NCl_3 slowly decomposed in the dark into nitrogen and chlorine and the latter remained dissolved in the carbon tetrachloride. On this account it was necessary to analyze the solution completely at the time of each experiment. In Berkeley a stock solution could be used for several weeks before it was necessary to discard it, but in connection with experiments performed in the summer at the University of Texas the decomposition was found to be much more rapid owing to the higher temperature. There were many indications that the decomposition was autocatalytic and became more rapid as the chlorine content increased.

Search for a Quantitative Reaction between NCl_3 and a Reducing Agent.—The chief problem in the analysis of the stock solutions for NCl_3 was to find a reducing agent which would react quantitatively with NCl_3 and yield only one derivative of the nitrogen. In the main reaction with a reducing agent NH_3 (or NH_4^+) is formed, and 1 mol NCl_3 reacts with 6 equivalents of the reducing agent; but the simultaneous formation of N_2 has been observed in some cases, corresponding to a reaction between 1 mol NCl_3 and 3 equivalents of the reducing agent. Since the latter reaction would render inaccurate an analytical method based on the determination of the amount of NH_3 formed, or of the reducing agent oxidized, the following experiments were performed to test for the formation of nitrogen in various reactions:

The apparatus used for this purpose consisted of a short cylindrical reaction chamber of about 100 cc. capacity, equipped with stopcocks at the top and bottom, and with the delivery tube from a long-stemmed dropping funnel sealed in at the side and near the bottom of the chamber. The top of the reaction chamber was connected by means of a capillary tube to a manometer. In each experiment the reaction chamber was filled completely with the reducing agent through the dropping funnel. A measured volume of the carbon tetrachloride solution of nitrogen

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[1] Hentschel, *Ber.*, 30, 1792 (1897).

[2] Noyes and Lyon, THIS JOURNAL, 23, 460 (1901).

[3] Chapman and Vodden, *J. Chem. Soc.*, [1] 95, 138 (1909).

[4] Raschig, *Chem. Ztg.*, 31, 926 (1907), has prepared NH_2Cl by the action of equimolal quantities of NH_3 and hypochlorite in alkaline solution.

[5] Gattermann, *Ber.*, 21, 751 (1888).

trichloride, and then a little free CCl_4 was drawn from the dropping funnel into the reaction chamber by gradually lowering the pressure in the manometer. The carbon tetrachloride remained at the bottom of the chamber below the entrance from the funnel, and the reducing agent was forced back into the funnel as nitrogen gas was evolved. The nitrogen was finally measured in the manometer and the per cent. of the nitrogen of the NCl_3 that had been transformed into N_2 calculated. Excess of the reducing agent was present in all the experiments.

The evolution of some nitrogen was found to be the rule rather than the exception. The rate of the reaction was observed to increase when the reaction vessel was shaken, from which it was concluded that the reduction was rapid in the aqueous phase, and that the rate of diffusion of the NCl_3 from the carbon tetrachloride phase was the main factor in determining the time required for the completion of the reaction. The proportion of N_2 formed was found to depend upon the nature of the reducing agent used, upon its concentration, and in some cases upon the concentration of the acid in the aqueous solution. However, the results obtained in duplicate experiments were only approximately concordant (owing, doubtless, to the fact that two phases were present). Accordingly the quantitative results are not recorded in this paper, and these experiments were continued only until a reducing agent was found which converted the nitrogen quantitatively to ammonia.

This reducing agent was sodium sulfite solution, and in none of the experiments with excess of this reagent was an appreciable amount of nitrogen formed. In all other cases there was a considerable quantity of nitrogen: among the substances investigated were ferrous sulfate, hydrogen sulfide, arsenious acid, sodium arsenite in neutral solution, and potassium iodide in hydrochloric acid solution. The evolution of nitrogen in the reduction of liquid NCl_3 has been reported by Bineau;[1] a small amount with arsenious acid, and a larger amount with hydrogen sulfide solution. Chapman and Vodden[1] observed the evolution of nitrogen when a solution of NCl_3 in carbon tetrachloride was reduced with an acidified potassium iodide solution.

Analysis of the CCl_4 Solution of NCl_3 and Cl_2.—As the result of the above experiments the determination of the NCl_3 content of the stock solutions was based on the reaction between NCl_3 and sodium sulfite.

$$3Na_2SO_3 + NCl_3 + 3H_2O = 3Na_2SO_4 + 2HCl + NH_4Cl.$$

A measured volume of the stock solution was run into excess of a concentrated sodium sulfite solution and the mixture was stirred or shaken. After a few minutes the aqueous layer and the CCl_4 layer were separated, and the latter was washed with water. The aqueous layer and the wash-water were mixed and were usually diluted to a known volume in a

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[1] *Loc. cit.*

graduated flask. This solution or a definite fraction of it was made alkaline with sodium hydroxide and the amount of ammonia determined by distilling into acid as in the determination of nitrogen by the Kjeldahl method. From the number of mols NH_3 and the volume of the stock solution used the *molal concentration* of nitrogen trichloride was calculated.

The chlorine of the NCl_3 and the free chlorine were converted into chloride by the excess sulfite. The Volhard method was used in determining the chloride; occasionally in the alkaline solution after the determination of ammonia,[1] but in general in another portion of the solution obtained in the reduction with sulfite. It was found necessary to remove the excess sulfite, since otherwise some metallic silver was formed in the titration with silver nitrate solution; this was done by adding potassium permanganate to a faint pink color and removing the slight excess permanganate with a drop or two of dilute sulfite solution. The method was tested by experiments with NH_4Cl solution in the presence and absence of sodium sulfite. The *total chlorine* in a stock solution was calculated as gram atoms per liter.

The Equivalent Concentration of Free Chlorine in a stock solution was calculated by subtracting from the total chlorine three times the molal concentration of the nitrogen trichloride.

The oxidizing power of the stock solutions was not determined directly from the amount of sulfite used in the reaction on account of the action of oxygen of the air on the sulfite solution. Moreover a rather large excess of sulfite was used in all the experiments. It is possible, however, to calculate the equivalent concentration of the oxidizing agent in a stock solution from the above measurements, since this is equal to 6 times the molal concentration of NCl_3 plus the equivalent concentration of free chlorine. In terms of the experimentally determined quantities, the equivalent concentration of the oxidizing agent is equal to 3 times the molal concentration of NCl_3 plus the total chlorine.

Reaction of NCl_3 with Arsenious Acid and with Sodium Arsenite Solution.—The investigation of the reactions between NCl_3 and various reducing agents was continued by the following method: The NCl_3 concentration in the stock solution was determined by reduction with Na_2SO_3 and analysis for NH_3; at the same time other portions of the stock solution were treated with the reducing agent that was being studied, and the ammonia determined in the resulting solutions. The proportion of the nitrogen of NCl_3 that was transformed into nitrogen gas was calcu-

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[1] Recent experiments of Mr. C. M. Bouton at the University of California have shown that it is necessary to determine the chloride and ammonia in different portions of the solution, since during the distillation to obtain NH_3 some chloride is formed by the action of NaOH and Na_2SO_3 on CCl_4. This error is large when liquid CCl_4 is present, and it is not negligible even when no liquid CCl_4 can be seen.

lated from the difference between the amounts of ammonia found in the two cases. This method has the following advantage over the direct determination of the nitrogen previously described: several samples of the NCl_3 solution can be worked with simultaneously, and all the experiments in a series can be treated in the same way as regards shaking, etc.

In two series of experiments with 0.123 *N* H_3AsO_3 solution (concentration expressed in oxidation equivalents per liter), 5 cc. of a 0.105 molal nitrogen trichloride solution, which contained only a small amount of free chlorine, were used in each experiment.

The results summarized in Table I show the effect of varying the concentration of the reducing agent.

TABLE I.—EFFECT OF VARYING THE CONCENTRATION OF H_3AsO_3.

Expt. No.	Reducing agent. Name.	Reducing agent. Volume.	Water added.	% of N set free.
1	Na_2SO_3	Indefinite	....	None
2	0.123 *N* H_3AsO_3	35 cc.	None	7.7
3	0.123 *N* H_3AsO_3	35 cc.	10 cc.	14.6
4	0.123 *N* H_3AsO_3	35 cc.	20 cc.	14.6
5	0.123 *N* H_3AsO_3	35 cc.	30 cc.	25.3
6	0.123 *N* H_3AsO_3	35 cc.	40 cc.	32.0

The results in Table I show that by decreasing the concentration of arsenious acid about one-half, the per cent. of the nitrogen set free is increased nearly fourfold.

The experiments summarized in Table II were performed to determine the effect of varying the concentration of acid. Sulfuric acid was added in each of the experiments with H_3AsO_3 and its initial concentration is shown in the fifth column. The total volume of the aqueous phase was 100 cc. in each of these experiments.

TABLE II.—EFFECT OF VARYING THE CONCENTRATION OF ACID.

Expt. No.	Reducing agent. Name.	Reducing agent. Volume.	Total volume.	Concentration of H_2SO_4.	% of N set free.
1	Na_2SO_3	Indefinite	...	0	None
2	Sodium arsenite	35 cc.	100 cc.	0	8.7
3	0.123 *N* H_3AsO_3	35 cc.	100 cc.	0	22.8
4	0.123 *N* H_3AsO_3	35 cc.	100 cc.	0.2 *N*	25.3
5	0.123 *N* H_3AsO_3	35 cc.	100 cc.	0.4 *N*	37.9
6	0.123 *N* H_3AsO_3	35 cc.	100 cc.	0.6 *N*	36.1
7	0.123 *N* H_3AsO_3	35 cc.	100 cc.	0.8 *N*	36.1

The results of Expts. 3 to 7 show that the per cent. of nitrogen set free increases with the acid concentration, but that there is no effect beyond 0.4 *N*. In Expt. 3 no sulfuric acid was added but the concentration of acid must not be regarded as zero since acid was liberated during the reaction. For this reason Expt. 2 with a neutral solution of sodium arsenite prepared as directed by Washburn[1] is especially interesting.

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[1] Washburn THIS JOURNAL, 30, 31 (1905).

This solution contained both NaH_2PO_4 and Na_2HPO_4 and therefore the concentration of H^+ remained small throughout the reaction. The relatively small amount of N_2 obtained in this experiment furnishes the best evidence that the proportion of nitrogen set free increases with the acid concentration.

Many other experiments were performed with arsenious acid and sodium arsenite, but in no case were we able to prevent the evolution of nitrogen. Chapman and Vodden[1] studied the reduction of NCl_3 in carbon tetrachloride by excess sodium arsenite solution which contained sodium bicarbonate. They noted and made allowance for a small quantity of nitrogen that was evolved, but do not state its amount; it was presumably somewhat smaller than the amount found in Expt. 2, Table II, where the experimental conditions correspond closely with those in the bicarbonate solution. Hentschel[1] and Noyes and Lyon[1] used an arsenite-bicarbonate solution in analyzing their solutions of NCl_3 in benzene. The error that was introduced by neglecting the nitrogen evolved was probably too small to materially alter their results.

Reaction with Hydrogen Sulfide Solutions.—Experiments with excess of saturated solutions of hydrogen sulfide gave an average value of 5.5% nitrogen liberated as N_2, independent of the concentration of sulfuric acid present during the reaction. The fact that the effect of sulfuric acid is different from that in the H_3AsO_3 experiments indicates that this effect is specific for the different reactions with reducing agents.

Reaction with Potassium Iodide Solutions.—In the experiments with potassium iodide solutions acid was added since alkali, which favors the formation of nitrogen, is formed in the reaction. About 18% of the nitrogen was transformed into N_2 and there was no definite variation with the concentration of sulfuric acid or of potassium iodide.

In a special experiment in the reaction chamber previously described the NCl_3 solution was introduced into a solution of potassium iodide in concentrated hydrochloric acid. The experiment was repeated several times but an appreciable amount of nitrogen gas was formed each time. This experiment was based on the idea that the reaction

$$NCl_3 + 3H_2O = NH_3 + 3HClO$$

is rapid and reversible.[2] It was hoped that owing to the reaction of HCl with NH_3 and with HClO the NCl_3 would be converted into NH_4Cl and Cl_2, and that the formation of nitrogen gas might thus be prevented. The observation that about three times as much nitrogen was evolved

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[1] *Loc. cit.*

[2] Seliwanow, *Ber.*, 27, 1012 (1894), claims that this is the case. He states that the reaction between HClO and NH_4Cl is rapid but does not go to completion, and that NCl_3 is rapidly converted by hydrochloric acid into Cl_2 and NH_4Cl, but dissolves only slightly in sulfuric acid.

when a neutral solution of potassium iodide was used was at first thought to support this theory of the mechanism of the reaction, but the evidence is inconclusive on account of the fact that the solution became alkaline during the latter experiment.

Hentschel[1] expressed the opinion that on account of the hydrolysis equilibrium of NCl_3, referred to above, the reactions of NCl_3 in aqueous solution would be identical with those of hypochlorous acid. The evolution of nitrogen in the above experiments with reducing agents shows that this conclusion is not completely correct. On the other hand our experiments must not be considered as disproving the existence of the hydrolysis equilibrium.

Other Reactions.—When *iodine* was introduced into a carbontetrachloride solution of NCl_3, nitrogen and the chlorides of iodine were rapidly formed. On the addition of a little water to the resulting solution a precipitate of iodic acid appeared.[2] This result supported the suggestion of Chapman and Vodden[3] that the presence of iodine facilitates the evolution of nitrogen in the reaction between NCl_3 and iodide in acid solution.

Whenever a solution of *sodium hydroxide* was brought into contact with a solution of nitrogen trichloride in carbon tetrachloride, nitrogen was evolved moderately rapidly. In order to determine if this was a quantitative reaction a solution of NCl_3 of known concentration was treated with excess NaOH and the resulting solution was analyzed for NH_3. 7% of the nitrogen was found as NH_3, which showed that 93% had been converted into N_2. For the sake of completeness the rapid reaction between NCl_3 and concentrated NH_4OH solution may be mentioned,

$$4NH_3 + NCl_3 = N_2 + 3NH_4Cl,$$

although we did not study it quantitatively.

Portions of a stock solution of NCl_3 were treated with aqueous solutions of salts of *hydrazine* and of *hydroxylamine;* nitrogen gas was evolved rapidly in both cases but no quantitative experiments were performed.

Hydrochinone was found to be oxidized to its hexachloro compound, which was identified by its crystalline form and melting point. *Urea* in acid solution apparently did not react with NCl_3 but nitrogen was evolved slowly with a neutral solution.

While the above experiments with sulfite, arsenious acid and sodium hydroxide were in progress the resulting aqueous solutions were tested for nitrate and for chlorate, with negative results. We also failed to obtain any test for nitrous acid (with urea) or nitric acid in water which

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[1] Hentschel, *Ber.*, 30, 1434 (1897).

[2] The formation of iodic acid in the reaction between iodine and NCl_3 was observed by Seliwanow, *loc. cit.*

[3] *Loc. cit.*

had been standing in contact with a carbon tetrachloride solution for several hours.[1]

Reaction between Aqueous Solutions of NCl_3 and NH_4Cl.—In connection with experiments with chlorine gas, which are described in the following article, some NCl_3 was prepared in aqueous solution by the action of excess of a dilute solution of ammonium chloride on gaseous chlorine. The observation of Noyes and Lyon, that the volume of nitrogen obtained in the reaction between Cl_2 gas and a 2% NH_4Cl solution is only 1 or 2% of the volume of the chlorine used, was confirmed in several experiments. It was observed, however, that N_2 gas continued to come off slowly from the final solution when this was allowed to stand. As the rate of evolution of N_2 seemed to be greater than could be accounted for by the decomposition of NCl_3 the possibility of a reaction between NCl_3 and NH_4Cl was considered. The following experiments were performed to determine if, in accordance with this explanation, the rate of the follow-reaction was increased when the concentration of NH_4Cl was increased.

Chlorine gas was generated by allowing 6 *N* HCl to drop on a concentrated solution of calcium permanganate. The chlorine was freed from hydrochloric acid by passing it through water and was dried by passing it through concentrated sulfuric acid.

A graduated glass tube such as is used in the Hofmann lecture experiment was filled with chlorine gas at atmospheric pressure. The gas was allowed to flow through the tube until that which escaped was completely absorbed by a concentrated solution of sodium hydroxide. An ammonium chloride solution of known concentration was allowed to flow into the tube until the tube was half-full. (In the first three experiments a smaller unmeasured volume was used.) After a known interval of time water was allowed to flow into the tube and the volume of the nitrogen measured at atmospheric pressure. In all the experiments except the first two the tube was immersed in a trough of water to prevent the entrance of air, and was covered with a black cloth to prevent the action of light on the nitrogen trichloride. The experiments were performed at room temperature (about 20°) and it was thought unnecessary to correct the gas volumes for changes in temperatures and atmospheric pressure. The results of some of the experiments performed are given in Table III.

Expts. 1 and 2 show that the chlorine reacts very rapidly with NH_4Cl solution and that only a small amount of nitrogen is evolved in this stage of the reaction. Expts. 3, 4 and 5 show that the evolution of N_2 in a

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[1] W. A. Noyes, THIS JOURNAL, 35, 767 (1913), has recently attempted to prepare an "electromer" of NCl_3, which would hydrolyze to give nitrous acid and hydrochloric acid.

TABLE III.—EVOLUTION OF N_2 IN REACTION BETWEEN Cl_2 AND NH_4Cl AND IN THE FOLLOW-REACTION BETWEEN NCl_3 AND NH_4Cl.

Expt. No.	Vol. of Cl_2.	Conc. of NH_4Cl.	Volume of N_2.	Time.
1	183.8 cc.	2%	1 or 2 cc.	in 1 minute
2	183.8 cc.	13%	4.0 cc.	in 1 minute
3	183.8 cc.	13%	21.5 cc.	in 3 hours
4	183.8 cc.	13%	17.5 cc.	in 1 hour
5	183.8 cc.	6%	60.5 cc.	in 24 hours
6	143.5 cc.	6%	46.5 cc.	in 24 hours
7	143.5 cc.	6%	48.0 cc.	in 24 hours
8	143.5 cc.	6%	47.5 cc.	in 24 hours
9	143.5 cc.	6%	47.0 cc.	in 24 hours

follow-reaction is easily observed in 6% or 13% NH_4Cl solution. Since this reaction is extremely slow when a 2% solution is used its speed must increase rapidly with the concentration of the ammonium chloride. Expts. 5 to 9 show that this reaction is practically complete within 24 hours in 6% NH_4Cl and that the final volume of the nitrogen is $^1/_3$ that of the chlorine used. The two reactions are evidently

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl \qquad \text{(fast)}$$

and

$$NH_4Cl + NCl_3 = N_2 + 4HCl. \qquad \text{(slow)}$$

In these reactions acid is formed and the concentration of H^+ increases greatly during each experiment. In order to determine if the concentration of H^+ has any marked influence on the rate of formation of N_2 in the follow-reaction a series of experiments was performed in which solutions of constant NH_4Cl concentration and varying initial HCl concentration were used. The amount of nitrogen evolved in a given time was found to be practically the same in all experiments. It follows that in this reaction the NCl_3 reacts directly with ammonium ion and not with the ammonia which is present at an extremely small concentration in equilibrium with ammonium ion and hydrogen ion.

Summary.

Nitrogen trichloride is conveniently prepared by the Hentschel method from hypochlorous acid and ammonium chloride solutions in the presence of an inert solvent. Solutions in carbon tetrachloride can be preserved in the dark for several weeks before they are greatly contaminated with chlorine formed by the decomposition of the trichloride.

Only one reducing agent was found, sodium sulfite solution, which reduces the nitrogen trichloride quantitatively to ammonia and chloride. The analytical methods were based on this reaction.

In the case of the other reducing agents investigated some nitrogen is evolved in a side reaction. These were ferrous sulfate, arsenious acid, sodium arsenite, hydrogen sulfide, and potassium iodide in acid solution.

Nitrogen trichloride decomposes rapidly with evolution of nitrogen

in the presence of sodium hydroxide. The reaction is not quantitative; some ammonia is also formed.

Nitrogen trichloride reacts slowly with dilute ammonium chloride solution and more rapidly with a concentrated solution to give nitrogen and hydrochloric acid.

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THE REACTIONS BETWEEN CHLORINE AND AMMONIA.

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The reactions between chlorine and ammonia in aqueous solution furnish striking examples of changes in the nature of the products which result from variations in the experimental conditions.

1. Nitrogen trichloride is formed very rapidly and almost quantitatively in the following reactions when excess of a strong acid is present:[1]

$$NH_3 + 3Cl_2 = NCl_3 + 3H^+ + 3Cl^- \qquad (1a)$$

$$NH_4^+ + 3Cl_2 = NCl_3 + 4H^+ + 3Cl^- \qquad (1b)$$

$$NH_4^+ + Cl^- + 3HClO = NCl_3 + H^+ + Cl^- + 3H_2O \qquad (1c)$$

The first two reactions are evidently closely related, and the third one is to be regarded as practically identical with the second on account of the rapid hydrolysis equilibrium for chlorine: $Cl_2 + H_2O = HClO + H^+ + Cl^-$. Thus in the experiments with hypochlorous acid and ammonium chloride chlorine would form unless the reaction between HClO and NH_4^+ is faster than the reaction between HClO and HCl. Similarly in the experiments with chlorine hypochlorous acid will form unless the chlorine reacts with NH_4^+ faster than it can react with water.[2] In the final solution, which contains NH_4^+, H^+ and Cl^-, there is a slow follow-reaction, $NCl_3 + NH_4^+ = N_2 + 4H^+ + 3Cl^-$, which has been discussed in the final section of the preceding article. Its speed increases with the concentration of the ammonium chloride and with the temperature.

2. When excess of a base is present nitrogen gas is evolved rapidly and almost quantitatively in the following reactions:

$$2NH_3 + 3Cl_2 = N_2 + 6H^+ + 6Cl^- \qquad (2a)$$

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4^+ + 6Cl^- \qquad (2b)$$

$$2NH_3 + 3ClO^- = N_2 + 3Cl^- + 3H_2O \qquad (2c)$$

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[1] For references see the first section of the preceding article.

[2] For a number of reactions of the halogens in aqueous solution there is evidence that the primary reaction is the hydrolysis of the halogen and that the hypohalous acid is a more reactive sustance than the halogen. See Bray, *Z. physik. Chem.*, **54**, 463, 497 (1906). However, these reactions involve the addition of oxygen, *e. g.*, the oxidation of arsenious acid by iodine, and the theory was not intended to apply to substitution reactions. In the present instance we have no means of deciding whether Cl_2 or HClO is the more reactive substance.