

It is possible that the salt effect may be used in certain cases to produce definite hydrogen ion concentrations with certain buffers where the buffer mixtures alone do not cover the  $P_H$  value desired.

**Remarks.**—A few difficulties connected with the work here described may be mentioned. When small quantities of buffer were used the colors were often dimmed by the action of carbon dioxide from the air before the e. m. f. could be measured. Moreover, in the course of the first experiments, extending over about 3 weeks, a slow drift toward the acid side was detected about the third week in the solution serving as the constant standard color for comparison, so that the results were not as concordant as they might have been and were therefore discarded. Whether this was caused by fading of the indicator in the solution serving as standard color, by evaporation of the stock solution of indicator, or by changes in the stock buffer solutions could not be ascertained. It may have been due to all 3 causes. Fresh color standards made up like the first were slightly redder and gave slightly higher  $P_H$  values. By starting with a standard having a given  $P_H$  value, however, the curves shown in Fig. 2 were constructed before any changes could be detected. Under any circumstances it is probably advisable to keep the standard tubes in the dark when not in use in order to avoid the bleaching action of light. It is not certain that the indicator suffers no change over long intervals but it certainly does not fade out entirely.

It may be noted that to reproduce definite  $P_H$  values the dilution of a given borate buffer mixture must be controlled as well as the proportions of boric acid and borax, and the amount of salt.

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## THE REACTION BETWEEN CHLORINE AND AMMONIA, II.<sup>1</sup>

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Some years ago one of us, working with A. B. Lyon,<sup>2</sup> showed that a considerable amount of nitrogen trichloride may be formed by the action of chlorine on a dilute solution of ammonia. An equation representing a somewhat complicated reaction was given to account for the result obtained and in the discussion it was suggested that in this reaction, and probably in others which are not usually considered as ionic, molecules separate into positive and negative parts as they react.

W. C. Bray and C. T. Dowell<sup>3</sup> have pointed out that the complicated,

<sup>1</sup> Abstract of a thesis submitted to the University of Illinois in partial fulfillment of the requirements for the degree of Master of Science.

<sup>2</sup> Noyes and Lyon, *THIS JOURNAL*, 23, 460 (1901).

<sup>3</sup> Bray and Dowell, *ibid.*, 39, 907 (1917).

ninth order reaction which was proposed is highly improbable and demonstrated that the nitrogen and nitrogen trichloride formed in Lyon's experiments were formed in independent reactions. The discovery by Raschig<sup>1</sup> that chloroamine,  $\text{NH}_2\text{Cl}$ , is formed by the action of a hypochlorite on ammonia, taken with the experiments described in this and the following papers, render it almost certain that nitrogen trichloride results from a series of reactions analogous, in part, at least, to those which give carbon tetrachloride from methane.

The idea that there are positive and negative parts, either actually or potentially present in molecules, was already somewhat current in the minds of chemists<sup>2</sup> and after it had been given, quite independently, an electronic interpretation by J. J. Thompson,<sup>3</sup> it has been an important factor in many discussions which have appeared in our literature. The questions involved are so fundamental that it seems desirable to accumulate new experimental evidence with regard to the formation and decomposition of nitrogen trichloride, a compound in which the conduct of the chlorine atoms is abnormal and such as to indicate that the atoms are positive in character.

So far as we are aware, all observers except Bray and Dowell and ourselves have prepared nitrogen trichloride by the use of ammonium salts. This might lead to the conclusion that in the experiments described in our first paper chlorine acted upon the ammonium hydroxide in the solution and not upon ammonia. We have, accordingly, studied the interaction of anhydrous ammonia and anhydrous chlorine at low temperatures. We have tried the experiment under the following conditions: (1) in presence of carbon tetrachloride (11 experiments); (2) in presence of chloroform (3 experiments); (3) in presence of pentane (2 experiments); (4) without any solvent (3 experiments).

The chlorine and ammonia were weighed in the liquid state in small sealed bulbs. The chlorine was generated by dropping conc. hydrochloric acid on potassium permanganate. It was passed through a wash bottle containing water and through 2 wash-bottles containing conc. sulfuric acid. It was then condensed in a bulb surrounded with carbon dioxide snow and alcohol. The tube connected with the small bulb in which the chlorine was to be weighed was drawn out to a long, fine capillary which was bent over in such a manner that the end could be dipped in the liquid chlorine, while the small bulb was cooled with carbon dioxide snow in alcohol. After a little of the chlorine had been drawn over and condensed, the bulb was removed from the cooling mixture and the

<sup>1</sup> Raschig, *Chem. Ztg.*, **31**, 926 (1907).

<sup>2</sup> Van't Hoff, *Z. physik. Chem.*, **16**, 411 (1895); Stieglitz, *THIS JOURNAL*, **23**, 796 (1901).

<sup>3</sup> *Phil. Mag.*, **7**, 237 (1904).

chlorine in it was allowed to evaporate and expel the air. By dipping the bulb into the cooling mixture a second time it was filled nearly full with liquid chlorine. The capillary tube was then sealed, and the bulb allowed to come to ordinary temperature for weighing.

Ammonia was prepared by warming a strong aqueous solution of the gas. It was dried by passing it through a U-tube surrounded with ice, through a tube containing soda-lime and another containing solid caustic potash. It was condensed and transferred to a bulb for weighing in the same manner as described for the chlorine.

Three different methods of bringing the chlorine and ammonia together were used. In the first experiments (1-6) a bulb having a capacity of 100 cc. and bearing a 3-way stopcock was filled about  $\frac{1}{3}$  full with carbon tetrachloride. After evacuating till the liquid boiled and the air was expelled the bulb was cooled with carbon dioxide and alcohol and one of the bulbs containing a weighed amount of chlorine and which had been cooled to a low temperature was attached to the tube from one arm of the 3-way stopcock and the chlorine was allowed to evaporate and condense in the carbon tetrachloride. The weight of chlorine used was determined by weighing the sealed bulb before it was cooled and opened, and weighing it again after the evaporation of the chlorine. After removing the bulb which had contained the chlorine, a bulb containing liquid ammonia was put in its place and the ammonia allowed to evaporate into the bulb containing the carbon tetrachloride and chlorine. Since considerable nitrogen is evolved from the interaction of the chlorine and ammonia, it was not always possible to introduce all of the ammonia, and losses sometimes occurred, causing unsatisfactory results (Expts. 2 and 6 in the table).

After the gases had been introduced, the bulb was connected with an exhausted bulb cooled with carbon dioxide and alcohol and the carbon tetrachloride and nitrogen trichloride were distilled over and condensed, the original bulb containing the ammonium chloride which was formed being finally heated to  $70^{\circ}$ . The amount of nitrogen trichloride formed was determined by shaking the distillate with sodium sulfite and determining the amount of ammonia formed by the reduction of the trichloride.<sup>1</sup> The amount of ammonium chloride formed was found in some cases by weighing the reaction bulb after the removal of the carbon tetrachloride and in other cases by dissolving the ammonium chloride in water and determining the ammonia and chlorine in the solution.

The second form of apparatus is shown in Fig. 1. The chlorine and ammonia were weighed in small bulbs, as before; these were attached to the stopcocks A and B, and, while they were still cooled with carbon dioxide snow and alcohol, the apparatus was filled with oxygen, the U-tube

<sup>1</sup> Dowell and Bray, *THIS JOURNAL*, 39, 898 (1917).

C was cooled with carbon dioxide and alcohol and a strong solution of sodium sulfite was placed in D. In one experiment with this apparatus (No. 11) no solvent was used, but glass beads were placed in the U-tube C. In other experiments chloroform, carbon tetrachloride or pentane

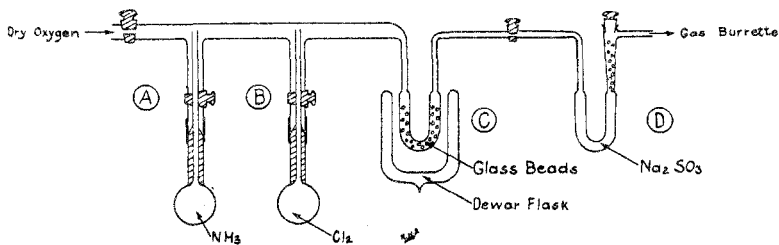


Fig. 1.

were used as solvents. The chlorine was allowed to evaporate and condense in the U-tube first, and then the ammonia. The nitrogen formed in the reaction was carried out by the current of oxygen and was determined after absorbing the oxygen in an alkaline solution of pyrogallol.

After the reaction had taken place and the amount of nitrogen formed had been determined, the contents of the U-tube in C was transferred to a suitable apparatus and distilled under diminished pressure, essentially as in the first method. A part of the nitrogen trichloride was found in this distillate and a part in sodium sulfite solution from D. The ammonium chloride formed was also determined. Expts. 7-12 were carried out in this manner.

In the third series of experiments (13-19) a bomb tube about 40 cm. long and 2 cm. in diameter was used. This was drawn out to a capillary and connected to a stopcock as shown in Fig. 2. The tube was exhausted to 10 mm. pressure or less and placed in a long Dewar tube and surrounded with solid carbon dioxide and alcohol. A weighed ammonia bulb was connected with A and the contents allowed to distil into the

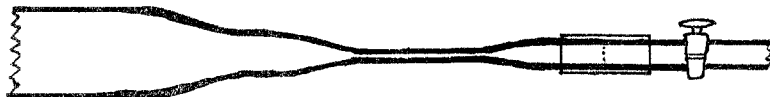


Fig. 2.

tube. A bulb containing carbon tetrachloride was then connected at A and the liquid allowed to distil into the tube, which was held at an angle of  $15^\circ$ . In this way, the tetrachloride was frozen along the side of the tube with the ammonia disseminated through it. The chlorine bulb was then attached and the chlorine was allowed to evaporate into the tube. The tube was then sealed at B, and placed in a horizontal position to warm up overnight.

Some of the earlier experiments of this series were carried out with the tube in a perpendicular position, the carbon tetrachloride being frozen on top of the ammonia. It was found with this arrangement that the gases had not thoroughly mixed, the ammonia not diffusing up through the carbon tetrachloride. On mixing the contents of the tube in the morning a further reaction took place with evolution of considerable heat.

In the morning, in those experiments (14 and 15) in which a rough estimate of the amount of nitrogen was made, a rubber tube connected with a gas buret set at 50 cc. was wired to the capillary tip and the tip was broken within the rubber tube, while the tube was immersed in ice-water. By taking account of the known capacity of the tube, of the rise or fall of the water in the buret and of the vapor pressure of carbon tetrachloride at 0°, the amount of nitrogen was calculated, approximately. The determination of nitrogen was only a rough approximation in either series.

The tube was then cut off and the carbon tetrachloride was filtered through a Gooch crucible into a solution of sodium sulfite. The various determinations were made essentially as in the other experiments.

The following table, for ease of comparison, the quantities involved in the experiments have been recalculated in their relation to 4 mols of ammonia. The actual quantities used were from 0.66 to 3.67 g. of chlorine and from 0.17 to 0.94 g. of ammonia.

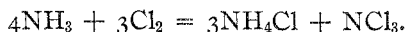
TABLE I.  
Results Calculated to 4 Mols of Ammonia.

Expt.	Form of apparatus.	Solvent.	Atoms Cl.	Mols NH <sub>4</sub> Cl.	Mols NCl <sub>3</sub> .	Atoms N.
1.....	1	CCl <sub>4</sub>	6.00	2.97	0.338	1.27
2.....	1	CCl <sub>4</sub>	6.08	1.11	0.137	...
3.....	1	CCl <sub>4</sub>	3.71	4.06	0.141	...
4.....	1	CCl <sub>4</sub>	6.14	3.19	0.134	...
5.....	1	CCl <sub>4</sub>	8.61	3.28	...	...
6.....	1	CHCl <sub>3</sub>	9.12	2.13	0.294	...
7.....	2	CHCl <sub>3</sub>	7.04	2.97	0.406	0.603
8.....	2	CHCl <sub>3</sub>	6.10	2.96	0.132	0.946
9.....	2	Pentane	8.00	2.48	0.156	1.016
10.....	2	Pentane	5.99	3.04	0.246	0.837
11.....	2	None	6.51	2.42	0.240	0.925
12.....	2	CCl <sub>4</sub>	6.00	2.99	0.333	0.911
13.....	3	CCl <sub>4</sub>	5.36	2.99	0.077	...
14.....	3	CCl <sub>4</sub>	6.59	2.98	0.070	0.826
15.....	3	CCl <sub>4</sub>	5.23	2.98	0.004	0.901
16.....	3	None	4.88	2.99	0.013	...
17.....	3	None	6.36	2.98	0.034	...
18.....	3	CCl <sub>4</sub>	10.54	2.92	0.165	...
19.....	3	CCl <sub>4</sub>	3.28	2.99	0.075	...

The temperature was —90° in all experiments except 8 and 9, in which it was —180°.

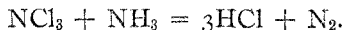
An examination of the table shows that the results obtained by the first method were erratic and of little value further than to show that considerable quantities of nitrogen trichloride may be formed by the direct interaction of chlorine and ammonia.

In the second series, with the exception of Expts. 9 and 11, the ratio of the mols of ammonia used to the mols of ammonium chloride formed is very closely 4 to 3. The ratios of the third series point still more closely to this value. These results indicate very clearly that the course of the reaction is expressed by the equation



The reaction doubtless occurs in steps (see the following paper) which rapidly succeed each other, with chloroamine,  $\text{NH}_2\text{Cl}$ , and dichloroamine,  $\text{NHCl}_2$ , as intermediate products.

The amounts of nitrogen trichloride formed are always far below those theoretically possible, either because a large part of the trichloride formed decomposes directly into nitrogen and chlorine or because it reacts with some of the ammonia



Since the hydrochloric acid formed would combine with ammonia until the latter was exhausted, neither the decomposition of the trichloride or its interaction with ammonia would affect the ratio between the mols of ammonia and mols of ammonium chloride as given in the first equation.

The fact that the ratio of the ammonia to the ammonium chloride is very nearly independent of the amount of chlorine used shows that the action of the chlorine is almost exclusively upon the ammonia and not upon the ammonium chloride. In Expt. 18, where a large excess of chlorine was used, there is a little indication that some of the ammonium chloride is attacked, but not much weight should be attached to the single experiment. Expt. 19 gives some indication of the interaction between nitrogen trichloride and ammonia, suggested above, since the amount of nitrogen trichloride formed is much less than in the preceding experiment, where an excess of chlorine was used.

#### Summary.

1. Anhydrous ammonia and anhydrous chlorine react to form nitrogen trichloride and ammonium chloride.
2. A considerable part of the trichloride always decomposes into chlorine and nitrogen, either directly or by interaction between the trichloride and ammonia.
3. The ratio of the mols of chlorine used to the mols of ammonia may be varied between wide limits without affecting, appreciably, the ratio between the mols of ammonia and the mols of ammonium chloride. This ratio is 4 to 3.

4. The chlorine reacts primarily with the ammonia. It reacts only to a trifling extent, or not at all, with the solid ammonium chloride which is formed.

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

### THE REACTION BETWEEN CHLORINE AND AMMONIA. III. PROBABLE FORMATION OF TRICHLORO- AMMONIUM CHLORIDE.

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With the exception of the experiments described in the preceding paper, and those of Bray and Dowell<sup>1</sup> and of Noyes and Lyon,<sup>2</sup> nitrogen trichloride seems always to have been prepared by the action of chlorine;<sup>3</sup> a hypochlorite,<sup>4</sup> or hypochlorous acid,<sup>5</sup> on ammonium chloride. Even those who have used chlorine have considered that hypochlorous acid is at first formed and that this acid then reacts with the ammonium salt.<sup>6</sup> The results described in the preceding paper demonstrate that nitrogen trichloride may be prepared by the direct interaction of chlorine and ammonia, in the absence of water. Experiments to be described in this paper show that nitrogen trichloride reacts quantitatively with hydrochloric acid, in the absence of water, giving ammonium chloride and chlorine. Also, when hydrogen chloride is passed into a solution of nitrogen trichloride in carbon tetrachloride<sup>7</sup> an immediate precipitation of ammonium chloride is caused.

In the light of these results it seems clear that the decomposition of nitrogen trichloride by hydrochloric acid is *not* an hydrolysis, under the conditions just described.

The most rational explanation of the formation of nitrogen trichloride from ammonium chloride seems to be that chlorine adds itself to ammonia, which is doubtless present in small amounts from the dissociation of the ammonium chloride to ammonia and hydrochloric acid. The chloro-

<sup>1</sup> Bray and Dowell, *THIS JOURNAL*, **39**, 905 (1917).

<sup>2</sup> Noyes and Lyon, *ibid.*, **23**, 460 (1901).

<sup>3</sup> Gattermann, *Ber.*, **21**, 751 (1888); Hentschel, *ibid.*, **30**, 1792 (1897); Chapman and Vodden, *J. Chem. Soc.*, **95**, 141 (1909).

<sup>4</sup> Hentschel, *Ber.*, **30**, 1434 (1897).

<sup>5</sup> Balard, *Ann. chim. phys.*, [2] **57**, 258 (1894); Hentschel, *Ber.*, **30**, 1792 (1897); Dowell and Bray, *THIS JOURNAL*, **39**, 896 (1917). Balard speaks of using other ammonium salts but gives no details. He also used a solution of ammonia.

<sup>6</sup> Seliwanoff, *Ber.*, **27**, 1012; Chapman and Vodden, *loc. cit.*

<sup>7</sup> This experiment was suggested by Professor Washburn in a conversation in which the author expressed the opinion that the decomposition of nitrogen trichloride by conc. hydrochloric acid is not an hydrolysis.