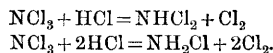


XX.—*Nitrogen Chloride.*

By DAVID LEONARD CHAPMAN and LEONARD VODDEN.

THE question of the true composition of nitrogen chloride possesses an especial interest for us on account of the observation made by C. H. Burgess and one of us that its vapour inhibits the photogenic interaction of chlorine and hydrogen. From the discrepant results of analyses carried out at different times over a period of almost a century on Dulong's explosive chloride, we were quite unable to decide whether this substance was the trichloride of nitrogen only, or a mixture (the composition of which depended on the mode of preparation) of this compound with compounds derived from ammonia by the partial displacement of hydrogen in the latter by chlorine. Unfortunately,

* And possibly also according to the equations :



no direct estimation of the hydrogen has ever been made. A sufficiently accurate idea of the degree of uncertainty at present attached to this question can be gained by reference being made to the following tabulated statement giving the formulæ calculated from the published analyses :

Authority.	Calculated formula.
Dulong (<i>Schweiggers J. Chem. Pharm.</i> , 1812, 8 , 32).	NCl_3 .
Davy (<i>Phil. Trans.</i> , 1813, 103 , 1, 242).	NCl_4 .
Porret, Wilson, and Kirk (<i>Gilb. Ann.</i> , 1814, 47 , 56, 59).	$\text{NCl}_{2.93}\text{H}_{1.09}$.
Bineau (<i>Ann. Chim. Phys.</i> , 1845, [iii], 15 , 82).	NCl_3 .
Gladstone (<i>Quart. Journ. Chem. Soc.</i> , 1854, 7 , 51).	$\text{N}_2\text{Cl}_5\text{H}$.
Millon (<i>Ann. Chim. Phys.</i> , 1838, 69 , 75).	Found that the liquid contained hydrogen.
Gattermann (<i>Ber.</i> , 1888, 21 , 752).	For the substance prepared in the presence of excess of ammonium chloride: I, $\text{NCl}_{2.4}\text{H}_{0.6}$; II, $\text{NCl}_{1.78}\text{H}_{1.22}$; III, $\text{NCl}_{2.68}\text{H}_{0.32}$. For the substance after long exposure to chlorine, $\text{NCl}_{3.3}$.
Hentschel (<i>Ber.</i> , 1897, 30 , 192).	For the substance prepared in the presence of excess of ammonium chloride: I, $\text{NCl}_{3.00}$; II, $\text{NCl}_{2.95}$; III, $\text{NCl}_{3.02}$; IV, $\text{NCl}_{2.91}$.

Half of the analyses indicate that the substance can contain an appreciable quantity of hydrogen; of the modern observers, Gattermann, whose results were accepted for many years, found that the whole of the hydrogen in ammonia could only be replaced by chlorine after long treatment of the oil with the latter element; but the more recent analyses of Hentschel are in entire disagreement with this view. The disputed point can only be satisfactorily settled by a

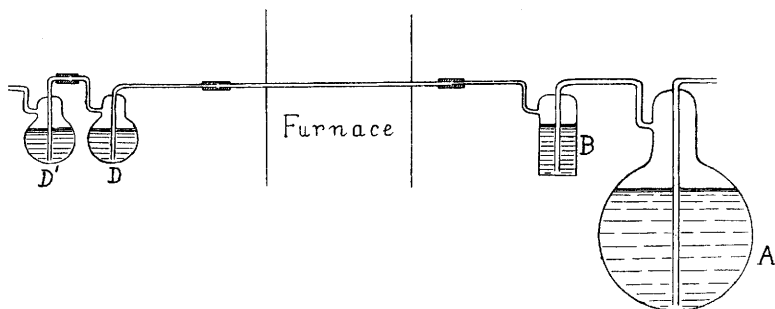
direct estimation of the hydrogen. This we have accomplished, and we find that the content of hydrogen is very small indeed, although the nitrogen chloride examined by us was prepared in the presence of a large excess of ammonium chloride. An independent estimation of the ratio of nitrogen to chlorine has confirmed this result.

Analysis of Nitrogen Chloride.

Estimation of the Hydrogen.—Chlorine gas was passed into a concentrated solution of ammonium chloride, and the aqueous solution of nitrogen chloride thus obtained was introduced into the flask *A* (Fig. 1).

A current of nitrogen carefully purified from oxygen was then passed through the solution, and the mixture of nitrogen and vapour of nitrogen chloride, after being dried, was passed through a quartz

FIG. 1.



tube heated to the highest temperature attainable with a Fletcher's fire-clay combustion furnace. The heated portion of the quartz tube was enclosed in a tube of glazed Berlin porcelain to prevent the furnace gases from coming into contact with the quartz, this material being pervious to hydrogen at high temperatures. Since in a quartz tube heated in the manner described, nitrogen chloride is completely destroyed, any hydrogen present in the vapour would appear as hydrogen chloride in the issuing gases. The wash-bottles *D* and *D'*, containing a neutral solution of potassium iodide, were attached to the end of the quartz tube after all the air in the apparatus had been displaced by nitrogen. The iodine liberated from the potassium iodide and the acquired acidity of the solution were, of course, respectively proportional to the hydrogen and available chlorine in the vapour. When a convenient quantity of iodine had been liberated—the depth of colour assumed by the solution being taken as a guide—the wash-bottles were detached, and their contents titrated with an *N*/10-

solution of sodium thiosulphate, the acidity being subsequently estimated with $N/100$ -potassium hydroxide, using phenolphthalein as indicator. The following amounts of the standard solutions were required:

30 c.c. of $N/10$ -sodium thiosulphate.

0.5 c.c. of $N/100$ -potassium hydroxide.

Whence we conclude that there is less than one atom of hydrogen to every three hundred atoms of chlorine in nitrogen chloride prepared in the presence of a concentrated solution of ammonium chloride.

A similar result was obtained when the vapour of nitrogen chloride, together with the small amount of nitrogen resulting from its decomposition in the solution, was drawn through the heated quartz tube and then through the potassium iodide solution with a Sprengel pump, the apparatus having been suitably modified for the purpose.

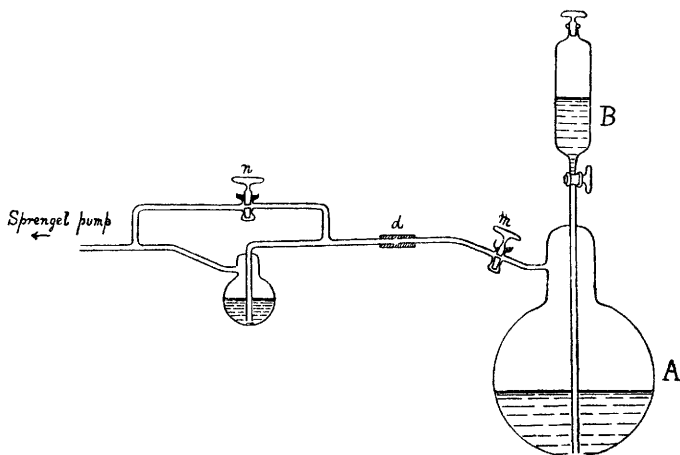
Estimation of the Ratio of Nitrogen to Chlorine.—The ratio of nitrogen to available chlorine was determined in a solution of nitrogen chloride in carbon tetrachloride, in which solvent the nitrogen chloride is remarkably stable.

A solution of nitrogen chloride in pure carbon tetrachloride was prepared in the following way. About 150 c.c. of carbon tetrachloride in a separating funnel were covered with a layer of a concentrated aqueous solution of recrystallised ammonium chloride. Chlorine gas was passed into the solution of ammonium chloride, the resulting nitrogen chloride being dissolved in the carbon tetrachloride by shaking the latter vigorously with the aqueous solution. The operation was repeated several times until the carbon tetrachloride had assumed a bright yellow colour.* The heavy solution of nitrogen chloride in carbon tetrachloride was then separated from the aqueous ammonium chloride and washed four or five times with distilled water. The analysis was performed with the apparatus depicted in Fig. 2. The yellow solution of nitrogen chloride was introduced into the funnel *B* after the air in the flask *A* (which contained a known volume of a standard solution of sodium arsenite) and in the rest of the apparatus had been completely removed by a Sprengel pump, not shown in the figure. When the taps *m* and *n* had been closed, most of the solution of the chloride of nitrogen in *B* was cautiously admitted into the flask *A*. The yellow solution was shaken with the standard sodium arsenite until the former had completely lost its colour, the flexible rubber joint at *B* permitted of this being done. The small amount of nitrogen evolved during the operation, together with some

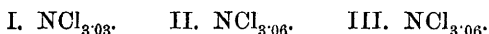
* The tint of a solution of nitrogen chloride in carbon tetrachloride is indistinguishable from that of a solution of chlorine in the same solvent.

carbon dioxide derived from the sodium hydrogen carbonate in the standard arsenite solution, was pumped out of the apparatus through an acidified solution of potassium iodide contained in the wash-bottle *C*, and collected. That the nitrogen chloride had been completely reduced by the sodium arsenite was proved by the circumstance that the potassium iodide in *C* was not discoloured while the gases were being withdrawn. The gas collected at the pump was measured and analysed, an allowance being made for the vapour pressure of carbon tetrachloride; it was found to contain, in addition to nitrogen and carbon dioxide, a minute trace of oxygen, which was ignored in the final calculation, since its amount was so small that a correction made for it on any conceivable hypothesis to account for its presence would have been negligible in comparison with the other errors of experi-

FIG. 2.



ment. The residual arsenite and the ammonia* contained in the flask *A* were also estimated. From the amounts of arsenite destroyed and ammonia and nitrogen produced, the formula of nitrogen chloride was calculated on the assumption that chlorine and nitrogen are the only components of that compound. Three experiments furnished results, from which the following formulæ were calculated :



From the results of two earlier experiments, in which a solution of

* Nitrogen chloride is reduced by sodium arsenite almost entirely to ammonia, whereas a relatively large proportion of nitrogen results from its reduction by an acidified solution of potassium iodide. In the latter case, the liberated iodine appears to facilitate the direct decomposition of the nitrogen chloride into its constituent elements.

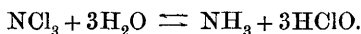
potassium iodide was employed to decompose the nitrogen chloride in the place of a standard arsenite solution, the following formulæ were calculated :



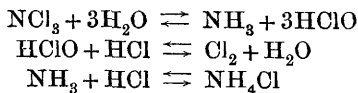
From the above results we conclude that nitrogen chloride prepared by the action of chlorine on a neutral solution of ammonium chloride contains little, if any, hydrogen, and that the nitrogen and chlorine are present in the proportion of one atomic weight of nitrogen to three of chlorine.

The Hydrolysis of Nitrogen Chloride.

Seliwanoff (*Ber.*, 1894, 27, 1012) has shown that several facts relating to nitrogen chloride can be more clearly understood if it is postulated that in aqueous solution the substance is hydrolysed according to the equation :



Thus, the extreme ease with which nitrogen chloride is reduced to ammonia receives an intelligible explanation, and the fact that the apparent solubility of nitrogen chloride in aqueous hydrogen chloride is greater than in sulphuric acid or in water is satisfactorily explained, for hypochlorous acid, one of the products of hydrolysis, is destroyed by hydrogen chloride, but is not affected by sulphuric acid. So far, the evidence adduced in support of the view that nitrogen chloride is hydrolysed in solution according to the above equation has been of an indirect character. We have accordingly carried out a simple experiment with the object of demonstrating the formation of ammonium salts from nitrogen chloride by hydrolysis alone. The experiment was conducted in the following way. A concentrated solution of nitrogen chloride in carbon tetrachloride was shaken in a flask of moderately concentrated hydrochloric acid, whereby, if Seliwanoff's view is right, ammonium chloride and chlorine should be formed according to the following equations :



and the chlorine, being soluble in carbon tetrachloride, should be removed and an excess of ammonium chloride left in the aqueous layer. The carbon tetrachloride was then separated, and the nitrogen chloride removed from the aqueous solution at the pump. The acid solution was next rendered alkaline by the addition of ammonia-

free potassium hydroxide, and distilled. The distillate contained a considerable quantity of ammonia the presence of ammonium chloride in the aqueous layer being thereby demonstrated.

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