dium trichloride. It is insoluble in aqueous hydrochloric acid, but is soluble in hot oxidizing acids forming hydrated pentoxides.

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REACTIONS OF COMPOUNDS WITH EVEN NUMBERS OF ELECTRONS. NITROGEN TRICHLORIDE AND NITROGEN TETROXIDE

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Some years ago it was suggested[1] that if we assume that the pair of electrons forming a covalence remain with one of the atoms which separates during a chemical reaction, a reconciliation between the positive–negative theory of the reactions of non-electrolytes and Lewis's theory of shared electrons could be effected. A further, very important, reconciliation between the older valence theories and Lewis's theory, has been furnished by the sharp distinction between doubled covalences and semipolar unions given us by Sugden's parachor,[2] and by the optically active sulfoxides of Phillips and his co-workers.[3]

In the first paper referred to it was pointed out that compounds having a covalence may, in reactions, separate either into electrically neutral parts, each with an odd electron, or into positive and negative ions by the method suggested above. Coleman and Howells[4] have shown that nitrogen trichloride reacts with butylene in the latter manner, the positive chlorine going to the end carbon atom.

In an extensive study of the reaction between nitric oxide, which has an odd electron, and nitrogen trichloride, it has been shown[5] that the nitric oxide takes an electrically neutral chlorine atom, with an odd electron, from the trichloride, leaving the ephemeral compound, nitrogen dichloride, also with an odd electron.

Nitrogen tetroxide is a compound containing only paired electrons, although it begins to dissociate to two molecules of nitrogen dioxide, each with an odd electron, at temperatures below zero. It has seemed of interest, therefore, to study the reaction of this compound with nitrogen trichloride.

It was expected that the reaction would prove to be a typical covalence reaction, the positive chlorine ion going to the negative oxygen, the nega-

[1] W. A. Noyes, THIS JOURNAL, **45**, 2959 (1923).

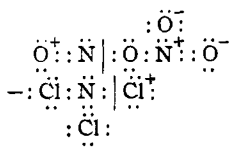
[2] Sugden, *J. Chem. Soc.*, **127**, 1525 (1925).

[3] Phillips, *ibid.*, **127**, 2552 (1925); Harrison, Kenyon and Phillips, *ibid.*, 2079 (1926).

[4] G. H. Coleman and H. P. Howells, THIS JOURNAL, **45**, 3084 (1923).

[5] *Ibid.*, **50**, 2902 (1928); **52**, 428 (1930); **53**, 2137 (1931).

tive dichloride ion (not the electrically neutral dichloride with an odd electron) combining with the positive nitric oxide ion to form the same dichlorodinitrogen oxide which was formed in the reactions of nitric oxide. At the temperatures it was necessary to use, the dichlorodinitrogen oxide decomposes at once to chlorine and nitrous oxide, as in the former experiments.



In the majority of the experiments tried the nitrogen tetroxide was condensed in the reaction bulb described in the former papers, the external bulb, in which nitric oxide was condensed for experiments at −150°, being omitted to secure a direct contact with the cooling solutions and give a better temperature control. With the nitrogen tetroxide at −80°, a cooled solution of nitrogen trichloride in chloroform was added, the bulb was evacuated and allowed to warm up slowly to −45° or above. When a solution containing 25% of the trichloride was used the reaction sometimes became very rapid, almost explosive, at −35°. There appears to be no appreciable reaction at −80°. At −45 to −35° the reaction proceeds slowly, with little change in color and a slow evolution of nitrous oxide and then of chlorine. After a time the solution became red from the formation of nitrosyl chloride.

The products of the reaction were distilled through the series of seven U-tubes and were separated and analyzed as for the experiments with nitric oxide and nitrogen trichloride, previously described. The results varied between wide limits and conditions for a smooth, fairly quantitative reaction have not been found. It does not seem worth while, therefore, to give the results of individual experiments. Fifteen or more experiments were tried under varying conditions. The following products have been found:

Nitrogen and Oxygen.—The compound, $:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}:\overset{:\ddot{O}:^{-}}{\ddot{N}^{+}}:\underset{..}{\ddot{O}}$, supposed to be one of the initial products of the reaction seems to decompose to oxygen and nitryl chloride, NO_2Cl. The larger part of the nitrogen trichloride always decomposed to nitrogen and chlorine. The gases not condensed in a U-tube surrounded by liquid air were analyzed and found to contain 95 to 96% of nitrogen and 4 to 5% of oxygen. It was thought at one time that chlorine monoxide might be formed. Some qualitative indications of its presence were seen in a few experiments but no satisfactory evidence was secured.

Nitrous oxide was always found. The amount varied from 0.03 to

0.44 mol for each mol of nitrogen tetroxide used. The largest amount was found in an experiment in which about 2.9 mols of nitrogen tetroxide was used with 29 mols of nitrogen trichloride. In other experiments the quantities found were much smaller.

Chlorine.—Nearly all the nitrogen trichloride decomposed to nitrogen and chlorine and none of the trichloride was found at the end of any experiment. This is in marked contrast with the conduct of nitric oxide reported in other papers. This may have been partly due to the higher temperature necessary to bring about any interaction between the trichloride and tetroxide but probably also because of some catalytic effect of the nitrogen tetroxide and dioxide on the trichloride.

Nitrosyl chloride was found in varying amounts. A number of different explanations may be given for this but without better experimental evidence it is useless to speculate.

Nitryl chloride, NO_2Cl, was found several times among the products of the reaction. The following analysis demonstrated its presence: gas, 1.51 mg. mol.; wt., 0.1146; N, 1.46 mg. at.; Cl, 1.59 mg. at.; O, 2.36 mg. at. This corresponds to mg. mol., Cl_2, 0.05; NO_2Cl, 0.90; NOCl, 0.56.

For a discussion of the existence of nitryl chloride see the following paper.

Nitrogen tetroxide was partly left unchanged at the end of the experiments.

Summary

1. The interaction of nitrogen trichloride dissolved in chloroform and nitrogen tetroxide, at 0 to −35°, gives nitrogen, oxygen, nitrous oxide, chlorine, nitryl chloride and nitrosyl chloride. The nitrogen trichloride is all decomposed and the nitrogen tetroxide is, in part, either unchanged or regenerated in the reaction.

2. The formation of nitrous oxide is most simply explained by supposing an initial covalence reaction in which the positive $\ddot{\underset{..}{\text{O}}}::\ddot{\text{N}}^{+}$ group combines with the negative $:\ddot{\text{Cl}}:\ddot{\text{N}}\vdots^{-}$ to form the same dichlorodinitrogen oxide which
$\quad :\underset{..}{\ddot{\text{Cl}}}:$
is formed by the interaction of nitric oxide and nitrogen trichloride. Nitrous oxide is formed from this by the loss of chlorine.

3. Nitryl chloride, NO_2Cl, is another product of the reaction.

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