[Contribution from the Chemical Laboratory of the University of Illinois]

THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND NITRIC OXIDE AT −150°. II. FURTHER EVIDENCE FOR THE FORMATION OF NITROGEN DICHLORIDE AND OF MONO-OXYGEN-DINITROGEN-DICHLORIDE

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In a paper published two years ago[1] it was shown that at −80°, in a solution of chloroform and carbon tetrachloride, two moles of nitric oxide react with one mole of nitrogen trichloride, giving one mole of nitrosyl chloride, one of nitrous oxide and two atoms of chlorine

$$2NO + NCl_3 = NOCl + N_2O + Cl_2$$

This was explained by assuming that the nitric oxide, having an odd electron, takes an atom of chlorine with an odd electron from the nitrogen trichloride to form the nitrosyl chloride. This leaves nitrogen dichloride with an odd electron and the latter combines with another mole of nitric oxide to form mono-oxygen-dinitrogen-dichloride, $O{=}N{-}NCl_2$. This last compound dissociates at −80°, giving nitrous oxide and chlorine. It was also found that at −130 to −140°, in petroleum ether, the reaction corresponds to the equation

$$NCl_3 + NO = N_2O + 3Cl$$

probably because hydrochloric acid formed by the action of nitrogen trichloride on the petroleum ether catalyzes a reaction between the nitrosyl chloride first formed and nitrogen trichloride, giving nitrous oxide and chlorine. It should be remarked, however, that this equation represents the final result of at least three or four reactions which occur consecutively or simultaneously.

To simplify the conditions and to eliminate, as far as possible, the catalytic effect of the hydrochloric acid and the reactions between nitrosyl chloride and nitrogen trichloride and between nitric oxide and chlorine, the reactions have been carried out in the presence of chloroform and carbon tetrachloride at −150°, the boiling point of nitric oxide.

Experimental Part

The apparatus used, shown in Fig. 1, was the same as that described in the first paper except that the bulb, F, in which the reaction was carried out, was surrounded with a second bulb sealed to it as shown in Fig. 2. Nitric oxide from a glass gasometer containing about 12 liters was condensed in the outer bulb by immersing it in liquid air. In some cases the solution containing a known amount of nitrogen trichloride was introduced by distilling it under low pressure from a glass bulb in which it had been frozen before

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[1] Noyes, This Journal, **50**, 2902 (1928).

connecting it with the apparatus at E. As the mixture distilled into the reaction bulb F, which was kept in liquid air, it froze on the walls of the bulb. In other cases the solution was allowed to flow slowly through a fine capillary tube down the inner wall of F. The latter method is considered better. This gave a large reacting surface for the mixture, and as the freezing point of nitrogen trichloride is lower than that of the mixture of chloroform and carbon tetrachloride, the trichloride was largely on the outside of the surface of the crystals of the solvent.

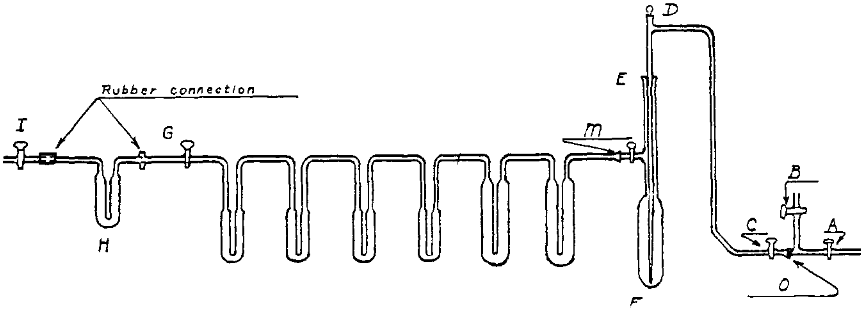


Fig. 1.—Ground-glass joints at O, E and M.

After evacuating the bulb, introducing nitrogen and evacuating again three or four times to remove the air, the liquid air was lowered away from the outer bulb containing liquefied and frozen nitric oxide. By proper adjustment of the cylinder containing the liquid air, the nitric oxide in the outer bulb was allowed to evaporate slowly back into the gasometer. In this manner a constant temperature of approximately −150° could be maintained almost indefinitely.

A measured quantity of nitric oxide was then slowly introduced through A and C (Fig. 1). The reaction, which did not always begin immediately, was apparent from the change in color of the mixture to the red color of nitrosyl chloride. After the desired amount of nitric oxide had been introduced, the mixture was allowed to stand for some time at −150° until the reaction was complete.

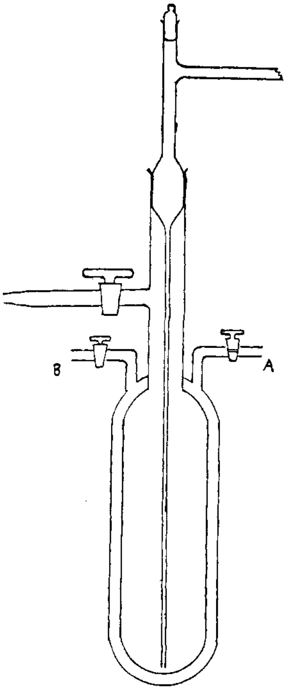


Fig. 2.

A large number of experiments at −150° have been carried through and various changes in the technique of separating the products of the reaction have been tried. The most important change has been measuring the nitrous oxide instead of weighing it. After fractionating the products and condensing the nitrous oxide in the U-tube H (Fig. 1), immersed in liquid air, the tube was connected with a tube leading to the bottom of a dry bottle and a tube from the top of the latter was connected to a bottle containing water in such a manner that as the nitrous oxide was allowed to evaporate, after removing the liquid air in which the U-tube was immersed, the air displaced passed into the second bottle and displaced its own volume of water. The water displaced was measured and thus the volume of the nitrous oxide was determined without allowing the gas to come in contact with water. Small amounts of nitrosyl chloride and chlorine present in the nitrous oxide were determined and proper corrections were made.

Two experiments at −80° were made to test the results given in the first paper by the new technique.

Attempts to carry out the reaction at the temperature of liquid air, −185 to −191°, have not been successful. After 11.9 millimoles of nitric oxide had stood in contact with the mixture containing an excess of nitrogen trichloride, at that temperature, for forty-five hours, 9.4 millimoles were recovered unchanged.

Results and Discussion.—From a large number of experiments, two at −80° and three at −150° have been selected as representing, approximately, the course of the reaction, which is distinctly different at the two temperatures.

TABLE I

RESULTS OF EXPERIMENTS

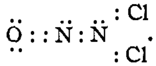
NCl_3 recovered	NCl_3 reacting	Molecular ratios				Temp., °C.
		NO	N_2O	NOCl	Cl	
0.04	1	1.96	0.71	1.01	2.20	−80
.23	1	2.42	.85	1.16	1.5	−80
.32	1	2.94	.72	1.70	0.16	−150
.33	1	3.10	.92	2.10	.60	−150
.23	1	3.00	.95	1.70	.90	−150

The results at −80° confirm the equation given in the first paper, $NCl_3 + 2NO = NOCl + N_2O + 2Cl$, as representing, approximately, the reactions which take place at that temperature.

At −150° the results correspond, approximately, to the equation

$$NCl_3 + 3NO = 2NOCl + N_2O + Cl$$

The results at −80° were explained by assuming that nitric oxide, having an odd electron, takes a chlorine atom with an odd electron from the nitrogen trichloride to form nitrosyl chloride. This leaves nitrogen dichloride, NCl_2, having an odd electron, which causes it to combine immediately with a second mole of nitric oxide to give mono-oxygen-dinitrogen-dichloride,



$\underset{\cdot\cdot}{\ddot{O}}::\ddot{N}:\ddot{N}\begin{matrix}:Cl\\ \\ :Cl\end{matrix}$. Because of the oxygen combined with one of the nitrogen atoms, this compound seems to dissociate to nitrous oxide, $\overset{-}{:}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\overset{+}{\mathrm{N}}:::\mathrm{N}:$ and chlorine at −80°.

It seemed difficult, at first, to explain the formation of *two* moles of nitrosyl chloride at −150°, but further consideration has led to the conclusion that the mono-oxygen-dinitrogen-dichloride is sufficiently stable to maintain a brief existence at −150° and that it yields a second atom of chlorine with an odd electron to a second mole of nitric oxide, forming the second mole of nitrosyl chloride. This would leave mono-oxygen-dinitrogen-monochloride, $\underset{\cdot\cdot}{\ddot{\mathrm{O}}}::\ddot{\mathrm{N}}:\underset{\cdot}{\ddot{\mathrm{N}}}:\mathrm{Cl}$. This would dissociate to nitrous oxide and chlorine, either at once or during the subsequent distillation of the products.

The course of the reaction at −80° shows that nitric oxide and chlorine combine very slowly to form nitrosyl chloride at that temperature and the second mole of nitrosyl chloride is very unlikely to have come from that combination.

Summary

1. At −150° the interaction of nitrogen trichloride and nitric oxide proceeds, approximately, according to the equation

$$\mathrm{NCl_3 + 3NO = 2NOCl + N_2O + Cl}$$

2. This equation is thought to represent the result of four successive reactions which may be represented by the equations

$$\mathrm{Cl}:\underset{\ddot{\mathrm{Cl}}}{\ddot{\mathrm{N}}}:\mathrm{Cl} + {}^{\cdot}\ddot{\mathrm{N}}::\mathrm{O} = \mathrm{Cl}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} + \mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\mathrm{Cl}$$

$$\mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\mathrm{Cl} + {}^{\cdot}\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \begin{matrix}\mathrm{Cl}:\\ \\ \mathrm{Cl}:\end{matrix}\ddot{\mathrm{N}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

$$\begin{matrix}\mathrm{Cl}:\\ \\ \mathrm{Cl}:\end{matrix}\ddot{\mathrm{N}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} + {}^{\cdot}\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \mathrm{Cl}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} + \mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

$$2\mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \mathrm{Cl}:\mathrm{Cl} + :\mathrm{N}:::\overset{+}{\mathrm{N}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\overset{-}{:}$$

3. Attempts to isolate the intermediate products, nitrogen dichloride, mono-oxygen-dinitrogen-dichloride and mono-oxygen-dinitrogen-monochloride have not been successful.

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