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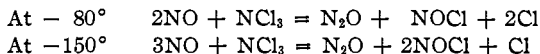
THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND
NITRIC OXIDE AT -150° . III. INTERACTION OF NITRIC
OXIDE AND CHLORINE AT -80 AND AT -150°

BY WILLIAM ALBERT NOYES

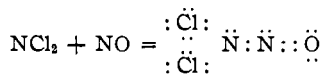
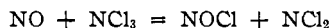
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In the papers already published¹ it has been shown that at -80 and -150° nitric oxide reacts with nitrogen trichloride chiefly in accordance with the equations



The difference in conduct of the compounds at the two temperatures was explained by assuming that the primary reactions, in both cases, are expressed by the equations



The difference in conduct at the two temperatures was explained in the second paper by assuming that the dichlorodinitrogen oxide formed in the second reaction is so unstable at -80° that it decomposes at once to nitrous oxide and chlorine, while at -150° it is sufficiently stable to yield a second atom of chlorine to the nitric oxide before it decomposes. It was also assumed that nitric oxide reacts more rapidly with dichlorodinitrogen oxide than it does with chlorine at -150° .

As it has not been possible to isolate either of the intermediate products, nitrogen dichloride and dichlorodinitrogen oxide, it has seemed desirable to obtain further evidence for their existence. This has been accomplished in three ways: by studying the reaction between chlorine and nitric oxide at -80 , -150 and -180° ; by using purified carbon tetrachloride instead of the mixture of chloroform and carbon tetrachloride as the solvent for the nitrogen trichloride; and by an improved technique in carrying out the reaction and in separating the products formed.

Chlorine and Nitric Oxide at -80 , -150 and -180° .—Eight to ten grams of carbon tetrachloride was frozen on the inner wall of the bulb shown in Fig. 2 of the last paper.² After immersing the bulb in liquid air, from 0.4 to 1.4 g. of chlorine was introduced through the long capillary tube of a small bulb in which it was weighed. The chlorine condensed and froze on the surface of the carbon tetrachloride. In the experiments at -80° the chlorine liquefied and ran to the bottom of the bulb when it

¹ Noyes, *THIS JOURNAL*, 50, 2902 (1928); 52, 4298 (1930).

² Noyes, *ibid.*, 52, 4299 (1930).

was warmed to that temperature or during the reaction with nitric oxide. In all experiments an excess of chlorine was used. In the first experiments the nitric oxide was completely converted to nitrosyl chloride within a few hours. In later experiments a rough determination of the rate of combination was made.

At -80° , 1.403 g. of chlorine (39.5 mg.-atoms) and 36.3 mg.-moles of nitric oxide were used. After thirty-three minutes from the beginning of the introduction of the nitric oxide only 7% of the latter was recovered uncombined.

At -150° , 1.402 g. of chlorine (39.5 mg.-atoms) and 35 mg.-moles of nitric oxide were used. In thirty-five minutes from the beginning of the introduction of the nitric oxide, 81% of the gas was recovered uncombined.

At -180° , 20.9 mg.-atoms of chlorine was frozen on the walls of the bulb without the use of carbon tetrachloride. After an hour and a half 67% of the nitric oxide was recovered uncombined. As some combination doubtless took place during the fractional distillation carried through the U-tubes to separate the nitric oxide from the chlorine and nitrosyl chloride, the combination which had occurred at -180° must have been less than 33% in one hour and a half.

Because of the difference in the physical conditions at -80 and at -150° , the results give only a rough approximation as to the rates of reaction at these two temperatures but the experiments show conclusively that nitric oxide and chlorine combine much more rapidly at -80 than at -150° .

To secure further evidence for the course of the reaction, thirteen new experiments have been carried out at -150° and nine at -80° , using carbon tetrachloride as the solvent for the nitrogen trichloride.

At the close of the reaction the bulb in which it was carried out contained six or seven substances: nitrogen, which boils at -196° ; nitric oxide, which boils at -150.3° ; nitrous oxide, which boils at -89.4° ; chlorine, which boils at -33.6° ; nitrosyl chloride, which boils at -5.4° ; nitrogen trichloride, which distils easily with carbon tetrachloride; and carbon tetrachloride, which boils at 76.8° .

It has been found advisable to carry out the operations in such a manner that by using an excess of nitrogen trichloride and waiting until the reaction is complete before distilling the products, no nitric oxide is left in the mixture to be distilled.

The U-tube, H,² which was connected to the set of U-tubes by rubber tubing in the experiments previously described, was replaced by a smaller U-tube sealed to the end of the system. This had a capacity of 18 cc. and was connected to a manometer, drying towers and a mechanical pump. When the system was exhausted and the connection between the drying towers and the pump was closed, on allowing the air in the

U-tube to pass into the system four times the manometer rose 30 mm. Hence 1 mm. on the manometer corresponded to 2.4 cc. of air. By allowing the nitrogen present at the end of an experiment to pass through the U-tube, immersed in liquid air to remove other gases, the rise of the manometer gave a rough determination of the amount of nitrogen present. This was always small in satisfactory experiments. It may have been present in the nitric oxide used or may have been formed by the decomposition of a little of the nitrogen trichloride.

The distillation of the other substances through the series of U-tubes is best carried out in a rather high vacuum and many tedious experiments have been tried and many analyses of products have been made to secure a quantitative determination of the course of the reactions.

In carrying out the separation the reaction bulb was at first surrounded with carbon dioxide snow in acetone while most of the nitrous oxide distilled into the first U-tube surrounded with liquid air. The nitrous oxide was then distilled to the second tube, also surrounded with liquid air. The liquid air was replaced around the first U-tube and an acetone bath at -50° placed around the reaction bulb. After a time the liquid air around the first U-tube was transferred to the third, the nitrous oxide in the second allowed to distil into that and the carbon dioxide-acetone mixture placed around the first tube. When a considerable part of the chlorine and nitrosyl chloride had distilled into the first U-tube, the reaction bulb was allowed to warm up slowly and the distillation of the chlorine and nitrosyl chloride continued till the latter was completely removed from the bulb as shown by the disappearance of the red color. The connection between the reaction bulb and the U-tubes was then closed and the nitrogen trichloride remaining in the former was later determined by methods which have been described. A little of the trichloride which distilled into the U-tubes with some carbon tetrachloride was unavoidably lost.

By distilling the nitrous oxide rather rapidly through the six U-tubes, using two Dewar cylinders containing liquid air, one with carbon dioxide snow and acetone and one with acetone at -50° , it was possible to bring the nitrous oxide into the last, 18-cc. U-tube, with only a little chlorine and nitrosyl chloride. By allowing this gas to evaporate into an empty bottle connected with a second bottle containing water, the water displaced from the latter gave a means of determining the number of moles of gas which had been condensed. The chlorine and nitrosyl chloride were absorbed in dilute sodium hydroxide. By determining the amounts of chlorine and nitrogen in aliquot portions of the solution the number of moles of each could be calculated. By subtracting the sum of these from the total moles of gas the moles of nitrous oxide were given.

In the experiments with chlorine and nitric oxide, it was necessary to use two empty bottles between the 18-cc. U-tube and the bottle of

water because the heat of the reaction between the nitric oxide and the oxygen of the air caused the nitrogen dioxide and tetroxide formed to mix with the air of the first bottle. The mixture, cooled as it passed into the second bottle, remained in the lower part of that, displacing only air to the bottle containing water.

After removing the nitrous oxide as described above, the residue of chlorine, nitrosyl chloride and carbon tetrachloride was distilled back to the first two U-tubes and the fractionation was repeated to concentrate the chlorine and nitrosyl chloride in the 18-cc. tube with only a little of the carbon tetrachloride. From this the two were distilled into a solution of sodium hydroxide and the chlorine and nitrogen were determined in the latter. The following reports of two experiments illustrate the degree of separation sometimes secured. The results are given in mg.-atoms and moles.

DEGREE OF SEPARATION OF SUBSTANCES PRESENT AFTER REACTION

Temp., -80° . Initial mg.-moles NCl_3 , 13.6; NO , 23.3

	N_2O fraction	NOCl fraction	NCl_3 fraction	Total
N_2O recovered (mg.-moles).....	8.1	8.1
Cl recovered (mg.-atoms).....	2.2	12.5	1.1	15.8
NOCl recovered (mg.-moles).....	0.6	12.5	...	13.1
NCl_3 recovered (mg.-moles).....	2.9	2.9

Temp., -150° . Initial mg.-moles NCl_3 , 18.4; NO , 35.3

	N fraction	N_2O fraction	NOCl fraction	NCl_3 fraction	Total
N (mg.-atoms)	1.6	1.6
N_2O	...	9.6	9.6
Cl	...	1.0	8.7	1.4	11.1
NOCl	...	0.3	21.8	...	22.1
NCl_3	7.2	7.2

Two experiments at -80° and three at -150° have been selected for the final report. The results were as follows.

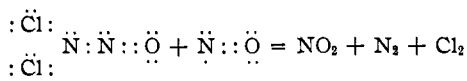
MOLECULAR AND ATOMIC RATIOS BETWEEN NITROGEN TRICHLORIDE, NITRIC OXIDE AND THE REACTION PRODUCTS

t, $^{\circ}\text{C}$.	NCl_3	NO	N	N_2O	NOCl	Cl
- 80	1	2.18	...	0.76	1.48	1.23
- 80	1	2.49	0.2	.86	1.57	1.25
-150	1	3.15	.15	.86	1.97	0.99
-150	1	3.38	.20	.82	2.20	.67
-150	1	3.59	.05	.85	2.39	.61

A further explanation of these results will be given later.

In one experiment at -150° , a slight leakage of air caused the formation of some blue nitrogen trioxide, N_2O_3 . This evidently reacted later with chlorine, forming nitrogen tetroxide and dioxide, N_2O_4 and NO_2 . These were separated quite completely by fractional distillation through the

U-tubes. This result made it seem possible that dichlorodinitrogen chloride may react with nitric oxide to form nitrogen dioxide, nitrogen and chlorine



To test this possibility, three experiments were carried through at -150° and 9 g. of the mixture of nitrosyl chloride and chlorine obtained was carefully fractionated for the presence of nitrogen dioxide. The ratio of nitrogen to chlorine in the last portion was 1:0.985. The amount of nitrogen dioxide present, if any, must have been very small.

Structure of Nitrous Oxide.—In the first paper¹ the electronic formula, $:\ddot{\text{N}}::\text{N}^+\ddot{\text{O}}^-:$, was proposed as probable. R. Mecke³ and C. P. Snow⁴ think that a linear formula with the oxygen between the two nitrogen atoms is indicated strongly by the infra-red spectra and the fact that the molecule has no electrical moment or only a very small one. In addition to the reasons given in the first paper, four facts about the chemical conduct of nitrogen seem inconsistent with such a formula.

(1) Nitrogen trioxide, N_2O_3 , nitrogen tetroxide, N_2O_4 , and nitrogen pentoxide, N_2O_5 , in which nitrogen atoms are held together by oxygen atoms, dissociate very easily, nitrogen trioxide almost completely, below zero.

(2) Lochte, Noyes and Bailey⁵ have shown that a double covalence between two nitrogen atoms in 2,2'-azobispropane, $(\text{CH}_3)_2\text{CH}:\text{N}::\text{N}:\text{CH}-(\text{CH}_3)_2$, is much more stable than a double covalence between carbon and nitrogen in the isopropyl hydrazone of acetone, $(\text{CH}_3)_2\text{CH}:\text{NH}:-\text{N}::\text{C}(\text{CH}_3)_2$. The stability of nitrous oxide, which dissociates only slightly even at 500° ,⁶ also points very strongly toward a union between the nitrogen atoms rather than to one between nitrogen and oxygen.

(3) The electronic structure of $\text{N}-\text{O}-\text{N}$ should be, in accordance with the rules for shared electrons,⁷ $:\ddot{\text{N}}:\ddot{\text{O}}:\ddot{\text{N}}:$. K. F. Schmidt⁸ has assumed a compound of similar structure, $:\ddot{\text{N}}:\text{H}$, as an intermediate in many reactions of hydrazoic acid, N_3H , but it is so reactive that it has not been isolated. If nitrous oxide has the structure suggested, it should also be very reactive. The comparative indifference of carbon monoxide weakens this argument, however.

³ R. Mecke, *Z. Physik.*, **64**, 173 (1930). A little earlier, *Z. physik. Chem.*, [B] **7**, 114 (1930), he suggested the formula $\text{N}\equiv\text{N}=\text{O}$, for chemical reasons.

⁴ C. P. Snow, *Proc. Roy. Soc. (London)*, [A] **128**, 294 (1930).

⁵ Lochte, Noyes and Bailey, *THIS JOURNAL*, **44**, 2557 (1922).

⁶ Berthelot, *Compt. rend.*, **77**, 1448 (1874).

⁷ Noyes, *Z. physik. Chem.*, **130**, 323 (1927).

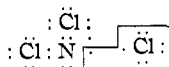
⁸ K. F. Schmidt, *Ber.*, **57**, 704 (1924).

(4) The formula N—O—N implies that both the trivalent nitrogen of the nitrogen trichloride and the bivalent nitrogen of nitric oxide have been changed to univalent nitrogen. Both chlorine and nitrogen trichloride are powerful oxidizing agents and such a result seems very improbable. The electronic formula of these papers represents one of the nitrogen atoms of nitrous oxide as trivalent and the other as quinquevalent. The quinquevalent nitrogen atom has one polar valence. This seems to be true of all quadrivalent or quinquevalent nitrogen atoms. This is clearly recognized for ammonium salts by everyone who does not claim that polar valences are not true valences. The parachors show that it is also true for nitro compounds, nitric acid, etc., which have a semipolar oxygen atom.

The discrepancy between the interpretations of the chemical and the physical evidence for the structure of nitrous oxide should lead us to hold our minds open for the present. Possibly some form of the old formula, which is, electronically, :N::N: , may reconcile the two views.



R. G. W. Norrish⁹ has recently found a photochemical reaction between nitrogen trichloride and chlorine which he explains by assuming that nitrogen dichloride is formed. The action of light on chlorine splits it into neutral atoms having odd electrons. Heat alone has the same effect at high temperatures:



Norrish's work offers very welcome support for the explanations offered in these papers.

Small losses of nitrogen, oxygen and chlorine were observed in nearly all experiments. Whether this was merely due to errors in the difficult and complicated technique involved or whether it may be due to other reactions or other compounds which have not been discovered is worthy of careful consideration by other experimenters who may find better methods of approach to the problem. It is not the intention of the author to continue the experiments further at the present time.

Summary

1. It has been shown that in the presence of carbon tetrachloride, nitric oxide and chlorine combine rather rapidly at -80° , much more slowly at -150° and, in the absence of any solvent, very slowly at -180° .

2. By means of experiments with a solution of nitrogen trichloride in carbon tetrachloride, further evidence has been obtained in support of the hypothesis that the primary reaction with nitric oxide gives nitrosyl

⁹ J. G. A. Griffiths and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A130**, 608 (1931).

chloride and nitrogen dichloride; that the dichloride combines with nitric oxide to form dichlorodinitrogen oxide; that this compound decomposes very rapidly at -80° but that it is sufficiently stable at -150° to yield a second chlorine atom to nitric oxide before it decomposes; and that this reaction is much more rapid than the combination of nitric oxide and chlorine at that temperature.

3. The rather rapid combination of nitric oxide with chlorine at -80° explains the excess of nitric oxide used and the excess of nitrosyl chloride found as compared with those required by the equation given. It also explains the deficiency of chlorine. The excess of nitric oxide and nitrosyl chloride and deficiency of chlorine at -150° may be explained in the same way or by supposing a further reaction of nitric oxide with a hypothetical monochlorodinitrogen oxide.

4. No satisfactory evidence was obtained that nitrogen dioxide is formed in the reactions studied.

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THE POSSIBILITY OF BIMOLECULAR ASSOCIATION REACTIONS

By LOUIS S. KASSEL

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It seems to have been first pointed out by Herzfeld¹ that the recombination of atoms to form a diatomic molecule could not be a bimolecular process, but must occur either on the walls or at triple collisions; Herzfeld calculated the mean life of the molecules which could result from simple collisions and obtained values of the order of 10^{-12} sec.; such a time is scarcely greater than the rather indefinite duration of a collision, which has, of course, exact meaning only after an arbitrary definition has been given. The details of this calculation might be changed slightly if it were to be repeated in the light of more recent knowledge, but the result would surely be unchanged. Furthermore, there is a considerable body of experimental material, all of which shows that diatomic molecules are not ordinarily formed at binary collisions.

There has been some tendency to generalize this statement and say that no bimolecular association reaction is possible, or at least that it will occur with only a negligible rate.² Now it is certainly true that bimolecular association reactions can occur, because this process is the reverse of unimolecular decomposition, and there are known some dozen reactions which are of this type, beyond any reasonable doubt. Such an argument

¹ Herzfeld, *Z. Physik*, **8**, 132 (1922).

² This view has been frequently expressed by H. S. Taylor and recently by Taylor and Emeléus, *THIS JOURNAL*, **53**, 562 (1931). It has been held by numerous other workers also.