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

The Reactions of Some Oxides of Nitrogen with Atomic Oxygen and Nitrogen

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In an investigation of the role played by the oxides of nitrogen in the nitrogen and oxygen afterglows, it was demonstrated that certain reactions were taking place between oxides of nitrogen and oxygen or nitrogen atoms, and, in two or three cases, at least, it was possible to estimate with a fair degree of accuracy the reaction probability per collision. The oxides of nitrogen involved were nitric oxide and nitrogen dioxide. At the pressures employed in the experiments, no appreciable amount of nitrogen tetroxide was present, and there was never any indication of the formation of nitrogen pentoxide. Nitrogen dioxide is frozen out in a liquid air trap, and if excess nitrogen dioxide is present, nitric oxide will condense out to form N_2O_3, but in the absence of nitrogen dioxide, nitric oxide will pass through a liquid air trap. It was shown that under the conditions of our experiments the reaction $2NO + O_2 = 2NO_2$ was too slow to produce a visible trace of nitrogen dioxide in a reasonable length of time, so that this reaction need not be considered. On the other hand, the atoms of oxygen or nitrogen are condensed on the walls in a liquid air trap, so that if nitric oxide is also present in the system a rapid reaction between nitric oxide and the atoms adsorbed on the walls of the trap is to be anticipated, and was undoubtedly observed in several instances.

In the experiments described herewith, the atoms of nitrogen or oxygen were produced by passing the gases through an electrodeless discharge produced in the usual manner, and the percentage dissociation was measured by a Wrede gage.[1] When the gases are pure and dry only a very slight dissociation may be observed, but when a per cent. or so of water or other impurity is added, 25–30% dissociation into atoms is readily obtained. The reason for the remarkable effect of small traces of impurities is not entirely clear, but it does not concern us in the present research.

The Reaction between Nitrogen Dioxide and Oxygen Atoms.—If nitrogen dioxide is introduced into a stream of oxygen gas which has been partially dissociated by an electrodeless discharge, a characteristic oxygen afterglow is obtained. This afterglow, which has been observed by numerous workers, will be discussed later. The afterglow at first increases in brightness as the proportion of nitrogen dioxide is increased, but on adding more nitrogen dioxide, the afterglow is suddenly quenched, and a considerable amount of heat is liberated at the point of mixing. With an excess of nitrogen dioxide, all the oxides of nitrogen are frozen out in the liquid air trap as a mixture of N_2O_3 and N_2O_4. The amount of nitric oxide was determined by measuring the amount of oxygen absorbed, and the total amount of oxides was determined by weight. The amount of water present was, in all cases, negligible. Data for this reaction are given in Table I. The only reaction possible under these conditions is

$$NO_2 + O = NO + O_2 \qquad \text{(I)}$$

Schumacher[2] has demonstrated that this reaction is probably rapid. From the data of a typical run (No. 3) one may calculate the reaction probability per collision using ordinary kinetic theory diameters for the atom and molecule. The reaction, judging by the heat evolved, is completed in a distance of 6 cm. from the point of mixing. The tube is 2.6 cm. in diameter, and the average temperature is estimated at 40°. The rate of flow is 130 cm. per second. Assuming the reaction to be 90% complete in a distance of 6 cm., one obtains a reaction probability of 10^{-5} per collision. This estimate is surely correct to the order of magnitude. The heat of activation for this reaction is certainly not very large. This reaction appears to be an excellent one for "titrating" the amount of oxygen gas that is dissociated into atoms.

TABLE I

Run	Total press., mm.	Press. H_2O	Mole O_2	Mole NO_2 introduced	Mole NO formed	Percentage diss. O_2
1	0.25	0	0.029	0.0108	0.00176	3.0
2	.25	0.0004	.019	.00542	.00204	5.4
3	.40	.013	.0075	.00945	.00372	25.0
4	.40	0	.0072	.00107	.00016	1.1
5	.48	.016	.0082	.0210	.00434	17.8

The Reaction between Nitric Oxide and Oxygen Atoms.—This is the reverse of the photochemical decomposition of nitrogen dioxide

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(1) Rodebush and Klingelhoefer, THIS JOURNAL, **55**, 130 (1933).

(2) *Ibid.*, **52**, 2804 (1930).

which has been studied by Norrish,[3] and by Dickinson and Baxter.[4] Mecke[5] concluded that the result of illuminating nitrogen dioxide by light of 3700 Å. was the decomposition by a predissociation into nitric oxide and a normal oxygen atom

$$NO_2 = NO + O \qquad (II)$$

Reaction II is followed by reaction I above, so that the yield is two molecules of nitric oxide per quantum. The recombination of II above, presumably by a triple collision

$$O + NO = NO_2 \qquad (III)$$

might be expected to give a molecule of NO_2 in an excited electronic state, with somewhat less than the critical energy of decomposition. This molecule might be expected to lose energy by radiation. Since this recombination takes place slowly, the reaction would be a typical "afterglow" reaction. When nitric oxide is introduced into pure oxygen gas which is partially dissociated, the "oxygen" afterglow is obtained. The greatest intensity is obtained with the highest percentage dissociation of the oxygen, and approximately equivalent amounts of nitric oxide. In order to obtain large percentages of atoms it is necessary to use moist oxygen, but a moderate afterglow can be obtained with dry oxygen, so that water does not play any role. There can be but little doubt that reaction III produces the afterglow, since it is impossible to imagine any other reaction under the circumstances. The oxygen afterglow which was first observed by Strutt,[6] when photographed with low dispersion consists of rather diffuse bands throughout the visible region with maximum intensity in the green. This region corresponds to the absorption region of nitrogen dioxide. Strutt would have postulated reaction III as the cause of the oxygen afterglow, but he was unaware of the existence of oxygen atoms. He postulated a reaction between nitric oxide and ozone; when this was tried no afterglow appeared. He was completely at a loss to account for this, and gave up the attempt to explain the afterglow. There is, of course, very little ozone under the conditions of our experiments.

The behavior of nitrogen dioxide fits in the above theory. If a small amount of nitrogen dioxide is introduced, nitric oxide is formed by a rapid reaction (I), and reaction III proceeds with an afterglow. If an excess of nitrogen dioxide is introduced, all the oxygen atoms are used up by I.

By increasing the pressure on the oxygen in which the afterglow is produced, the number of atoms is reduced and the number of triple collisions increased. With a pressure of 0.9 mm. the afterglow disappears completely about a meter from the discharge tube. This is presumably due to the exhaustion of the oxygen atoms. Under these conditions it is possible to freeze out both nitric oxide and nitrogen dioxide in the liquid air trap. In order to freeze out all the nitric oxide, as N_2O_3, it was found necessary to add nitrogen dioxide to the gas flow at the entrance to the liquid air trap, showing that the nitric oxide is present in larger amount than the nitrogen dioxide. This evidence proves that reaction III is taking place in the afterglow, and agrees with the hypothesis that III is slower than I. It should be possible by a series of determinations at different pressures to determine the rate of reaction III relative to reaction I, and to decide if it involves triple collisions.

The Reactions of the Oxides of Nitrogen with Nitrogen Atoms.—Nitrogen which has passed through the electrodeless discharge contains, in addition to atoms in the normal state, excited atoms, and molecules in the $^3\Sigma A$ level. Any of these species should react with the oxides of nitrogen, but we have assumed that all species other than the normal atoms are present in negligible amounts. We have no experimental evidence to justify this assumption. However, it seems probable that the *main* reactions are with normal atoms.

If nitric oxide or nitrogen dioxide is added in small amounts to active nitrogen, the characteristic afterglow (first positive bands) fades, and only a faint bluish glow is observed. On adding larger quantities, the typical oxygen afterglow appears. A further increase in the amount of nitrogen dioxide will quench the afterglow, but there is no change observed on further increasing the amount of nitric oxide. If the nitrogen is moist so that atoms are present in considerable amounts, then a considerable evolution of heat is observed on introducing either of the oxides of nitrogen, and we may assume that the reactions taking place are of the same order of rapidity as that of nitrogen dioxide and oxygen atoms. These reactions must be

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[3] Norrish, *J. Chem. Soc.*, 1158, 1604, 1611 (1929).

[4] Dickinson and Baxter, THIS JOURNAL, **50**, 774 (1928).

[5] Mecke, *Z. physik. Chem.*, **B7**, 108 (1930).

[6] Strutt, *Proc. Phys. Soc.*, **23**, 66 (1910); Stoddard, *Proc. Roy. Soc.* (London), **A147**, 464 (1934).

$$N + NO = N_2 + O \qquad (IV)$$
$$N + NO_2 = 2NO \qquad (V)$$

The reaction

$$N + NO_2 = N_2 + O_2 \qquad (VI)$$

is probably much slower. As soon as oxygen atoms are present, reactions I and III will begin, of course. With an excess of nitrogen dioxide the reaction is undoubtedly completed in the gas phase, and an analysis of the contents of the liquid air trap gives some information as to the amount of nitrogen atoms present as well as the rate of the reaction. The data are given in Table II. The calculated percentage dissociation is based upon the assumption that reactions IV and V are the only reactions that are taking place.

Table II

Run	Total press.	Press. H_2O	Mole N_2	Mole NO_2 introduced	Mole NO formed	Percentage diss. N_2
1	0.44	0.002	0.013	0.00782	0.00086	1.7
2	.50	.013	.010	.00382	.00112	2.8
3	.37	.0	.015	0	.00008	0

Conditions for the Disappearance of the Afterglow.—If an excess of nitrogen dioxide is added to either the oxygen or nitrogen afterglow, the afterglow disappears, due to the removal of all active species, and nothing is left in the gas mixture except the oxides of nitrogen and the elementary molecules. As has been mentioned before, however, either of the oxides of nitrogen in certain small amounts will extinguish the nitrogen afterglow. Furthermore, a mixture of nitrogen and oxygen in certain definite amounts gives no afterglow. Nothing condenses out in the liquid air trap from this non-luminous mixture which shows the absence of nitrogen dioxide. Furthermore, nitric oxide and oxygen atoms cannot both be present, since these would react on the walls of the trap to form the dioxide. There is reason to believe that both oxygen and nitrogen atoms are present so that we may conclude that this non-luminous mixture contains no oxides of nitrogen, the oxides having been destroyed by reactions IV and V. Furthermore, if nitric oxide is added to this dark mixture, a strong afterglow is produced. This fact completes the argument that the oxygen afterglow is due to reaction III and that the "dark" mixture of oxygen and nitrogen contains no oxides of nitrogen as a result of reactions IV and V.

Summary

The reaction $NO_2 + O = NO + O_2$ has been estimated to have a probability of 10^{-5} per collision at 40°.

The reactions $N + NO_2 = 2NO$ and $N + NO = N_2 + O$ are shown to be fairly rapid reactions.

The reaction $NO + O = NO_2$ presumably takes place by triple collision, and is accompanied by the oxygen afterglow.

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The Electric Moments of Alkyl Borates and Substituted Boric Acids

By M. M. Otto

Several investigators[1] have found dioxane a very satisfactory solvent for use in the determination of the electric moments of compounds. Wilson and Wenzke[1d] found that dioxane has the property of dissociating the double fatty acid molecules into single ones. They obtained moments for acetic and propionic acid comparable with the moments obtained by Zahn[2] for the acid at temperatures high enough to warrant the complete dissociation into single molecules.

The moments of the substituted phenylboric acids were desired. As they are not soluble enough in benzene, dioxane, in which they are very readily soluble, was selected as the solvent. There might, however, be a complication factor due to the tendency of boron to coördinate with oxygen as indicated by Bowlus and Nieuwland.[3]

Phenylboric acid, *n*-amylboric acid and *n*-butylboric acid are soluble enough in benzene so that their electric moments might be measured in both solvents. It was also possible to measure *n*-amyl borate and *n*-butyl borate in benzene and dioxane. With these data it should be possible to decide the value of dioxane as a solvent for substituted boric acids.

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(1) (a) Williams, This Journal, **52**, 1831 (1930); (b) Williams, *ibid.*, **52**, 1838 (1930); (c) Smyth and Walls, *ibid.*, **53**, 2115 (1931); (d) Wilson and Wenzke, *J. Chem. Physics*, **2**, 546 (1934); (e) Kumler and Porter, This Journal, **56**, 2549 (1934).

(2) Zahn, *Phys. Rev.*, **37**, 1516 (1931).

(3) Bowlus and Nieuwland, This Journal, **53**, 3835 (1931).