[Contribution from the Fixed Nitrogen Research Laboratory]

THE OXIDATION OF NITROGEN TETROXIDE BY OZONE

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The main purpose of this research was to determine the proportions in which gaseous ozone reacts with gaseous nitrogen tetroxide, to form the pentoxide.

Helbig[1] was the first to investigate the action of ozone upon nitrogen tetroxide. He showed that a gaseous mixture of the dioxide and tetroxide is bleached by the action of ozone, nitrogen pentoxide being formed, and described an excellent method by which this action could be utilized for the preparation of pure pentoxide.

Russ and Pokorny[2] utilized the catalytic decomposition of ozone by nitrogen pentoxide in making vapor-pressure measurements on the pentoxide, and showed that the decomposition of the latter was prevented so long as ozone is present. They also have utilized[3] the oxidation of nitrogen tetroxide to the pentoxide by ozone for the preparation of pure pentoxide.

Apparatus and Method.—Preliminary experiments were made by introducing successive small quantities of ozonized oxygen into a bulb containing a gaseous mixture of nitrogen dioxide and tetroxide. It was found that a point could thus be reached where the small quantity of ozone introduced would cause an almost immediate bleaching of the red-brown fumes of the dioxide. This demonstrated that nitrogen tetroxide is readily oxidized by ozone in the gaseous phase and that the reaction is for all practical purposes instantaneous. This immediately suggested a "titration" method for determining the proportions in which ozone and nitrogen tetroxide react, using the disappearance of the red color of nitrogen dioxide as an end-point. As far as known it is thought that this is the first time that "titration" in the gaseous phase has been employed.

The apparatus finally used (Fig. 1) consisted of two cylindrical tubes, *A* and *B*, 32 cm. long and 2.3 cm. in diameter, connected by a smaller tube carrying the stopcocks *c* and *d* and between these a glass pressure gage, *m*.[4] The ends of the Bulb *A* were blown clear so that a good observation tube was formed. It constituted the nitrogen tetroxide bulb and reaction chamber, while Bulb *B* was the ozone bulb. The volumes of Bulbs *A* and *B* were 117 cc. each.

These bulbs were immersed in a thermostat, consisting of a large cylin-

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[1] Helbig, *Atti accad. Lincei*, **11,** II, 311 (1902); *ibid.*, **12,** I, 211 (1903).

[2] Russ and Pokorny, *Monatsh.*, **34,** 1027 (1913).

[3] Ref. 2, p. 1051.

[4] This manometer is a modification of that described by Daniels and Bright, This Journal, **42,** 1131 (1920).

drical iron tank with a glass bottom. It was filled with water, which was always close to 25° and was brought exactly to 25° at the time of experiment. Looking downward, from above the thermostat, lengthwise through Tube *A* and the surrounding water, through the glass bottom and against an illuminated white plate, brown fumes in the tube could be detected in a very low concentration, and their point of disappearance quite accurately noted.

After evacuating the apparatus carefully, nitrogen tetroxide was introduced to the desired pressure measured by Manometer *m*. Then Stopcock *d* was closed and the tetroxide in the remaining parts of the apparatus with the exception of Bulb *A* was removed by evacuation and thorough washing with air.

Dry ozonized oxygen from a large storage cylinder *O*, at a pressure somewhat less than 1 atmosphere, measured with rough accuracy by the manometer *p*, was then introduced into Bulb B for use in carrying out the titration.

Analysis of the gas was made by means of the detachable analysis bulb *P*, the volume being known and the exact pressure of the gas in it being measured by the gage *m*. The analysis was carried out according to standard practice, that is, absorption in neutral potassium solution, acidification of the solution with dil. sulfuric acid, and titration of the liberated iodine against standard sodium thiosulfate solution.

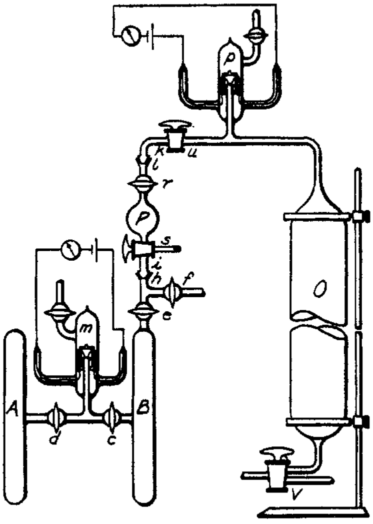

Fig. 1.

The pressure of tetroxide was very much lower than that of the ozonized gas so that titration could be carried out by letting the ozonized gas into the tetroxide. Titration was facilitated by the small capacity of the system between *c* and *d*. By closing *c* and opening *d* for a fraction of a second, the small portion of gas contained therein could be let into *A*. The process could be repeated, thus permitting the addition of ozone to the nitrogen tetroxide "drop by drop."

Preparation of Nitrogen Tetroxide.—The tetroxide was prepared by heating crystals of C. P. lead nitrate, and condensing liquid tetroxide in a tube immersed in an ice-salt bath. Since the crystals contain considerable moisture, a means for drying the gas before condensation had to be introduced.

The substance obtained was an orange-colored liquid, which became lighter in color as the temperature was lowered corresponding to the change in the equilibrium

$$\underset{\text{red brown}}{2NO_2} = \underset{\text{colorless}}{N_2O_4}$$

There was no evidence of any green color due to nitrogen trioxide.

Preparation of Ozone.—The ozone was obtained by liquefaction of ozonized oxygen from a Siemens ozonizer in a condenser immersed in liquid air, as described in the preceding article. The large cylindrical reservoir was evacuated, washed with oxygen and again evacuated, then filled to the desired pressure with oxygen and ozone by the necessary number of condensations and evaporations from the condenser into the reservoir. A very pure and dry oxygen-ozone mixture was in this way obtained in the reservoir, at a concentration depending upon the extent to which the liquid in the condenser was fractionated. In this work very concentrated ozone was not desired.

Calculation of Data.—The amount of tetroxide used in the titration was calculated from the volume of bulb A and the pressure and temperature of the gas. Allowance for the dissociation of the tetroxide into dioxide was made on the basis of Schreber's[5] expression for Natanson's[6] data on the equilibrium between these substances. With the help of Schreber's expression the following table was constructed for the partial pressure of dioxide at 25° in a mixture and at any desired total pressure. These results are also shown in the graph (Fig. 2), which is here reproduced for the convenience of others working in this field.

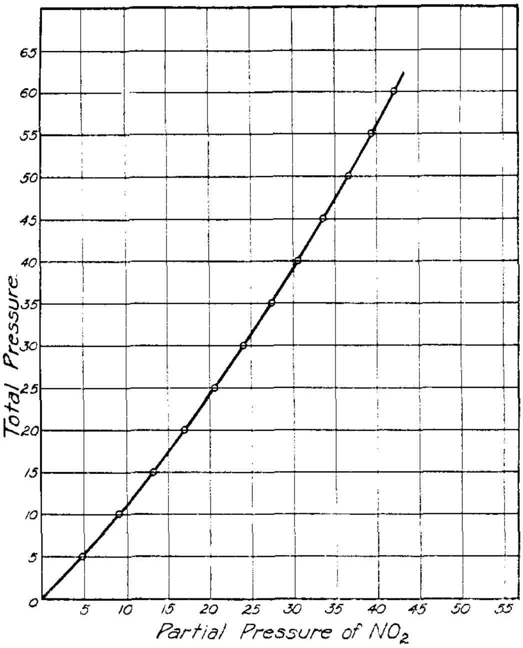

Fig. 2.

p_{total}	p_{NO_2}	p_{total}	p_{NO_2}	p_{total}	p_{NO_2}
5	4.77	25	20.63	45	33.49
10	9.14	30	24.05	50	36.40
15	13.21	35	27.33	55	39.22
20	17.02	40	30.47	60	41.95

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[5] Schreber, *Z. physik. Chem.*, **24**, 651 (1897).

[6] Natanson, *Wied. Ann.*, **24**, 454 (1885); **27**, 606 (1896).

The amount of ozone used was calculated from the analysis of the oxygen-ozone mixture, and the change in pressure in Bulb B.

Results.—Eight complete experiments were made as described above. The results are shown in the following table. The number of moles of tetroxide was taken as the total number of moles in the dissociated as well as in the undissociated form. The experiments were made in the order indicated by the experiment number but are arranged in the order of increasing percentage of ozone in the oxygen-ozone mixture.

Expt.	Ozone conc. % Vol.	Moles O_3 per mole N_2O_4	Expt.	Ozone conc. % Vol.	Moles O_3 per mole N_2O_4
8	2.37	1.07	1	7.32	1.06
7	2.44	0.98	5	8.15	1.26
6	2.89	1.07	3	11.89	1.57
2	5.95	0.97	4	17.04	1.41

At the lower concentrations, it appears within the accuracy of the data, that 1 mole of ozone reacts with 1 mole of tetroxide.

At concentrations above 8% a new phenomenon has apparently entered, causing the results to come out higher. This does not necessarily indicate, however, that more than 1 mole of ozone was actually required per mole of nitrogen tetroxide. It is well known that the potassium iodide method of analysis fails for concentrated gas, and gives irregular values that are usually too high.[7] These considerations appear to offer a logical explanation for the high values of ozone when concentrated ozone was employed.

Summary

The reaction between nitrogen tetroxide and ozone has been investigated at 25°.

The oxidation is practically instantaneous.

Quantitative measurements have been made titrimetrically using the disappearance of brown fumes as the indication of the end-point, thus performing a true titration in the gaseous phase.

Results show that 1 mole of ozone is required per mole of nitrogen tetroxide at 25°; thus 1 oxygen atom of the 3 in the ozone molecule is available in the oxidation at this temperature.

This is in striking contrast to the oxidation of sulfur dioxide to the trioxide by ozone at temperatures below 40° in which $^1/_3$ mole of ozone is required per mole of sulfur dioxide, all of the 3 oxygen atoms in the molecule being available in the oxidation.

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[7] See preceding article.