XXXVII. — *On the Reduction of the Oxides of Nitrogen by Metallic Copper in Organic Analysis.*

By W. THORP.

SOME years ago, in a paper published by Dr. Frankland ("Philosophical Transactions," vol. 147, page 63), some determinations of nitrogen in organic bodies by Dumas's method were given, in which it was found that a certain quantity of the nitrogen was evolved from the combustion-tube as nitric oxide, notwithstanding that a considerable quantity of metallic copper was placed in the anterior portion of the tube. The author states that—"It was found impossible to prevent the occurrence of a considerable amount of binoxide of nitrogen in the resulting gas. Even when it was made to stream over 12 inches of an intensely ignited mixture of copper turnings and copper reduced from the oxide, the resulting nitrogen still contained 10·9 per cent. of binoxide. It was, therefore, necessary to estimate the volume of the latter gas by means of solution of protosulphate of iron, and to deduct half its volume from the observed amount of the mixed gases. The presence of protoxide of nitrogen would not interfere with the accuracy of the result, as this gas is unaffected by solution of protosulphate of iron, and contains exactly its own volume of nitrogen."

These analyses having been conducted in the ordinary charcoal furnace, it appeared probable that the oxides of nitrogen might be decomposed by metallic copper under the influence of the superior temperature obtainable in Hofmann's gas combustion furnace. It was to decide this question that the following experiments were undertaken :—

Some thin bands of copper, about 3·5 mm. wide, obtained by passing stout copper-wire between rollers, were made into spirals, about 200 mm. in length, by twisting them round a glass rod. Two of these spirals, placed one within the other, were introduced into a piece of combustion-tube. Oxygen was next passed through the tube while heated to redness, in order to convert the copper superficially into oxide, which was afterwards reduced by a current of dry hydrogen. When the reduction was complete, the tube was allowed to cool, the stream of hydrogen being continued.

Before commencing each of the undermentioned experiments, the hydrogen was expelled by a stream of carbonic anhydride, and the conditions under which nitrogen determinations are usually made were, to a certain extent, obtained by mixing nitric oxide with about twice its volume of carbonic anhydride.

In experiments I and II, the copper was heated to bright redness, the mixture of nitric oxide and carbonic anhydride passed over it, and the gas issuing from the tube collected over mercury in a graduated receiver about 460 mm. in length, and about one-sixth filled with a strong solution of potassic hydrate. The flow of gas was so regulated that about two cubic centimetres were collected per minute.

After remaining for some time in contact with the alkaline solution, the volume of gas was read off, a measured quantity of oxygen added, and the mixture allowed to stand during several hours. The volume was again observed, and, no diminution having taken place, it was evident that the whole of the nitric oxide had been decomposed.

	I.			II.			
	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Gas collected	Oxygen added.	Mixture after adding oxygen.	
Observed volume ..	54·6	13·75	63·2	93·1	9·11	104	cub. cent.
Temperature of gas.	16°·5	16°·5	14°·8	21°	21°	18°·4	C.
Barometer	758·25	758·25	764·15	758·5	758·5	759·7	mm.
Temperature of do. .	16°·7	16°·7	13°·6	19°·6	19°·6	16°·9	C.
Aqueous column....	78	..	77	80·8	..	12·8	mm.
Mercurial	104	79·7	60	7	48·7	38	mm.

These numbers reduced to 760 mm. B. and 0° C. give—

	I.	II.	
Gas collected	42·639	82·252	c.c.
Oxygen added	11·299	7·683	„
	53·938	89·935	„
Vol. of mixture after adding oxygen	53·733	90·023	„
Difference	0·205	0·088	

III. Another experiment was made, in which the tube was

heated to dull but distinct redness, all other conditions being as in the previous experiments. On observing the volume after the addition of oxygen, a considerable absorption was found to have taken place. In order to ascertain the amount of oxygen absorbed, the residual portion was determined by means of pyrogallic acid.

	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Residue after adding pyrogallic acid.	
Observed volume ..	72·6	31·55	87	61·6	cub. cent.
Temperature of gas .	22°·8	22°·8	23°·2	24°·4	C.
Barometer	761·4	761·4	759·9	759·25	mm.
Temperature of do..	21°·4	21°·4	22°·6	23°·3	C.
Aqueous column ...	74	..	96	180·8	mm.
Mercurial „ ...	40·2	8·8	14·8	27·9	mm.

These numbers reduced to 760 mm. B. and 0° C. give—

Gas collected	60·789	cub. cent.
Oxygen added	27·933	„
	88·722	„
Vol. of mixture after adding oxygen	74·945	„
Volume absorbed	13·777	„
Residue after adding pyrogallic acid	51·597	„

By deducting this remaining nitrogen from the volume of the gas collected, we find that the latter contained 9·192 cub. cent. of nitric oxide. As this gas consists of equal volumes of nitrogen and oxygen, it follows that 51·597 of nitrogen was collected as such, and 4·596 as nitric oxide, that is, 8·179 per cent. of the nitrogen, in the gas acted upon, escaped reduction.

IV. In the next experiment, the mixture of nitric oxide and carbonic anhydride was passed so that about 4 cub. cents. were collected per minute, other conditions being the same as in experiments I and II.

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	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Residue after adding pyrogalllic acid.	
Observed volume...	66·1	25·84	83·9	64·2	cub. cent.
Temperature of gas.	21°·6	23°·3	23°	21°·8	C.
Barometer	764·65	763·5	762·6	762·05	mm.
Temperature of do..	20°·5	22°·6	21°·7	20°·3	C.
Aqueous column....	71·3	..	70·9	132	mm.
Mercurial „	63	25·3	17·8	101·3	mm.

These numbers reduced to 760 mm. B. and 0°C. give:—

Gas collected	54·147	cub. cent.
Oxygen added	22·363	„
	76·510	„
Vol. of mixture after adding oxygen	72·611	„
Volume absorbed	3·899	„
Residue after adding pyrogalllic acid	49·000	„
Nitric oxide in the gas collected ..	5·147	„

This corresponds to 4·99 per cent. of nitrogen as nitric oxide.

V. A last experiment was performed to ascertain the influence of a much larger proportion of aqueous vapour. For this purpose about 70 mm. of the posterior portion of the tube was filled with moistened asbestos; the gases were thus charged with water before coming in contact with the heated copper, the other conditions remaining as in experiments I and II.

	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Residue after adding pyrogalllic acid.
Observed volume...	57	24·55	74·4	54·2
Temperature of gas.	18°·2	18°·2	20°	21°·9
Barometer	752·75	752°·75	750·95	750·25
Temperature of do..	17°	17°	19°	20°·6
Aqueous column....	95·5	..	103·1	154
Mercurial „	78·3	32	8·6	30·9

These numbers reduced to 760 mm. B. and 0°C. give:—

Gas collected	45·425	cub. cent.
Oxygen added	21·286	„
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	66·711	„
Mixture after adding oxygen	64·861	„
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	1·850	„
Residue after adding pyrogalllic acid	45·085	„
Nitric oxide in the gas collected. . . .	0·34	„

This corresponds to 3·756 per cent. of nitrogen as nitric oxide.

This last experiment seems to show that the complete reduction of the oxide of nitrogen cannot be depended upon in an actual analysis where much aqueous vapour is usually present. But 3·756 represents the percentage of the *nitrogen* which escapes reduction, and in an actual analysis, even if the substance burnt contained 20 per cent. of nitrogen, the error would only be 0·75 per cent., which would not very materially affect the results.

The conclusion I would draw from these results is that at a moderate rate of speed, and at a high temperature, practically, the whole of the nitrogen is evolved as such in Dumas's method of determination.

These experiments were conducted in the laboratory of the Royal College of Chemistry, and under the kind superintendence of Dr. Frankland.