BAGSTER: THE REACTION BETWEEN

VIII.—The Reaction between Nitric Acid and Copper.

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On attempting to measure the volume of nitric oxide produced by the action of 5N-nitric acid on copper under certain conditions, it was found that when the gaseous products were evolved and passed into sodium hydroxide solution in a vacuum, complete absorption took place, although a considerable volume of nitric oxide should have been obtained (Higley, Amer. Chem. J., 1905, This reaction was investigated in the hope of throwing **17**. 18). further light on the reaction between nitric acid and copper. Veley (Phil. Trans., 1891, 182, 279) showed that the nitrous acid present was the cause of solution in dilute acid, and proposed a series of reactions involving the reduction of the nitrous acid to nitric oxide, followed by the oxidation of the nitric oxide to nitrous acid by the nitric acid. The work of Lewis and Edgar (J. Amer. Chem. Soc., 1911, 33, 292) shows that there is an equilibrium between nitric acid, nitric oxide, and nitrous acid, and that this equilibrium is but slowly attained. It seems unlikely, therefore, that in such case the nitric oxide would be completely and instantly oxidised, as would be necessary to secure complete absorption of the product in the experiment just described.

The following explanation of the process, in terms of wellknown electrochemical theory, is suggested: (1) oxidation of the hydrogen film on the copper by the nitrous acid, which itself is reduced to hyponitrous acid, the copper passing into solution to replace the hydrogen removed; (2) oxidation of the hyponitrous acid to nitrous acid by nitric acid, which itself is reduced to nitrous acid. It may be assumed that the first reaction will produce hyponitrous acid in unimolecular form $(H_2 + HNO_2 \rightarrow$ $H_2O + HNO'$), and as Divers (T., 1889, 75, 112) has shown that hyponitrous acid has the double molecule, it may be considered that at the moment of formation it will be in a reactive state corresponding with nascent hydrogen, and completely oxidised by nitric acid. It will be shown that the product of reaction with dilute acid is nitrous acid, produced in quantity necessary to satisfy the above scheme. It might be expected that sufficiently dilute nitric acid would fail to oxidise completely the hyponitrous acid formed, and in such case nitrous oxide, the well-known decomposition product of hyponitrous acid, should appear as a product.

This has been found to be the case by Higley (loc. cit.), using 3N and more dilute acid. It would not be expected that much nitrous oxide should be obtained; if the nitric acid were so weak that it failed to oxidise most of the hyponitrous acid, the reaction would cease when the nitrous acid originally present was exhausted. This has been found to be the case with N/2-nitric acid. Reaction started by addition of sodium nitrite ceased when the nitrous acid was destroyed, but could be restarted by the addition of more nitrite.

Divers (loc. cit.) has shown that nitrous acid oxidises hyponitrous acid, with the formation of nitric oxide and water, and in the course of the present work it was found that nitric oxide is the only gaseous product of reaction between copper and an excess of N/3-nitrous acid, prepared by adding sodium nitrite solution to excess of dilute hydrochloric acid. Here, hyponitrous acid formed would, in the absence of nitric acid, be oxidised by the excess of nitrous acid. As in the case of very dilute nitric acid, it would be expected that very dilute nitrous acid would also produce some nitrous oxide. This has been verified in the case of N/50-nitrous acid, prepared as above, reacting with an excess Nitric oxide was produced, but at the end of the reacof copper. tion the gas in solution was collected, and found to consist largely of nitrous oxide. The nitrous oxide was probably formed when the nitrous acid had become nearly exhausted. It is unlikely that the hyponitrous acid will be oxidised by nitrous acid in the presence of much nitric acid, as the nitrous acid in the neighbourhood of the copper will react with it, and conditions will consequently be favourable for oxidation of the product by the nitric acid, if present in quantity.

Further, Peters (Zeitsch. anorg. Chem., 1919, 107, 313) states that in the presence of carbon dioxide, a 5 per cent. solution of sodium nitrite reacts with copper, producing nitric and nitrous oxides, nitrate being formed in solution. Known constants for nitrous and carbonic acids show that about 0.25 per cent. of the nitrite will be present as free acid, which at this very small concentration will react with the copper in the manner already discussed, the same products being obtained. The nitrate would be formed by direct decomposition of the nitrous acid.

Reference should finally be made to the work of Ackworth and Armstrong (T., 1877, 32, 54), where it is shown that copper salts in solution give rise to an increased yield of nitrous oxide. These authors used a small volume of nitric acid, and it is probable that as the acid became used up, the nitrous acid accumulated in solution would react with the hyponitrous acid formed. A deep blue colour characteristic of complex copper salts was noticed when copper was dissolved in nitrous acid during the present work. This complex, in the case of Armstrong's work, would diminish the concentration of free nitrous acid, thus leading to the formation of a greater quantity of nitrous oxide.

So far, discussion has been confined to dilute acid. It has been shown (Ihle, Zeitsch. physikal. Chem., 1895, 19, 577) that nitric acid above 35 per cent. by volume will react in the absence of nitrous acid. This concentration corresponds with just under 8N. Reference to the table (p. 86) shows that such acid yields nitrogen peroxide as well as trioxide. As a secondary reaction is not apparent in the experiments described with dilute acid, it is probable that the products obtained from stronger acid nearly represent primary ones. The nitrogen peroxide may be regarded as the product of the direct oxidation process by the nitric acid, the nitrous anhydride also obtained in quantity from 8N- and 10N-acid being due to the simultaneous progress of both types of reaction.

EXPERIMENTAL.

When the experiment described at the beginning of this work was carried out quantitatively, it was found that the absorbing solutions contained nitrite corresponding with from 310 to 320 c.c. of N/10-permanganate for every gram of copper dissolved. This result was obtained with the product of reaction from acid of strength from 5N to 15N. The theoretical quantity of permanganate corresponding with the reactions discussed is 318 c.c., being the same whether the product is nitrous anhydride, nitrogen trioxide, or nitrogen peroxide. Nitrous acid, if formed, would be expected, under the conditions described, to distil as anhydride, owing to the equilibrium

$$2HNO_2 \equiv H_2O + N_2O_3$$
.

To distinguish between the possible products, it was necessary to determine the total nitrogen in the absorption vessel, apart from any that might distil there directly as nitric acid. For this purpose, the apparatus shown in the figure was constructed. Nitric acid was admitted after exhaustion to the vessel, A, containing the copper by means of the funnel, B. Nitric acid was condensed in C and returned to A. Gaseous products were absorbed in Dand E, which contained sodium hydroxide solution. Connexion with the mercury pump was closed by a tap during reaction. Tests with this apparatus in the absence of copper showed that no appreciable quantity of nitric acid distilled through the condenser when cooled to 10° .

In the course of preliminary tests, using 10N and weaker acid, it was found that when the condenser was cooled to 0° , nitric oxide was produced there, the effect being still slightly apparent at 10° with 6N-acid. The probable explanation is that, gaseous trioxide being a mixture, at the lower temperature the nitrogen peroxide is partly condensed, thus allowing the nitric oxide to pass on and through the alkali unabsorbed. This effect would at once be apparent in the case of trioxide; if excess of peroxide were also present, greater condensation would have to take place before the composition fell below that corresponding with trioxide, when



complete absorption would cease and nitric oxide appear. The production of nitric oxide will be accompanied by a diminished quantity of products in the absorption train.

In carrying out an experiment, the nitric acid was kept boiling, the temperatures shown in the table being the boiling points of the acid solutions in a vacuum. A slow stream of carbon dioxide was passed through the tube F to sweep the gaseous products from the condenser after removal of the acid vapour. For analysis, the nitrite in a portion of the absorption solution was determined with permanganate, and the total nitrogen in the residue estimated as ammonia by distillation with Devarda's alloy. A series of results is shown in the following table. In each case, 0.250 gram

		Nor-						Temper
	Nitric	mality		Nitrogen	Total	N ₂ O ₄ .	Nitrogen	ature of
No.	acid.	of	Temper	- as $N_{g}O_{a}$.	nitrogen.	Per	as NÕ.	conden-
	D.	acid.	ature.	Gram.	Gram.	cent.	Gram.	ser.
1	1.40	14.5	6 0°	0 ∙0553	0.0980	77		10°
2	1.40	14.5	60	0 ·0546	0.1001	80		10
3	1.30	10	45 - 50	0.0557	0.0616	10.2		10
4	1.30	10	45 - 50	0.0560	0.0630	11.0		10
5	1.30	10	45 - 50	0.0542	0·0 6 00	10.5		5
6	1.25	8	35 - 40	0.0542	0.0582	$7 \cdot 2$		10
7	1.20	6	30	0.0520	0·0 6 10	(10.8)		16
8	1.20	6	30	0.0490	0.0490		0.0045	10
9	1.50	6	30	0.0420	0.0423		0.0090	7
10	1.17	5	30	0·0546	0.0595	(9)		20

of copper was used, and at least ten times the quantity of acid needed for solution.

The theoretical quantity of trioxide to satisfy the reactions suggested is 0.0555 gram, the total nitrogen being the same when trioxide is the product, and twice the amount if peroxide is the only product.

The blank tests showed that in the case of experiments 1 to 6 there was no nitric acid distilled to make the total nitrogen value The small loss of nitrogen mentioned as occurring with the high. weak acid must still be considered as taking place, however, with the condenser at 10°. Although, as explained, this loss will not be apparent in the trioxide value, it will introduce an error of a few milligrams in the total nitrogen value. In the case of experiments 7 and 10, the value for the total nitrogen is higher than it should be; the copper in the case of the 6N-acid required a considerable time for solution, the acid occasionally "boiled with bumping," and unless the temperature of the condenser was as low as 10°, nitric acid reached the absorbers by direct distillation. Values such as are shown were repeatedly obtained, but it was not possible to secure a more definite result. As already indicated, the fact that the product from 5N- and 6N-acid more easily forms nitric oxide than that from 8N- and 10N-acid shows that it contains less peroxide. Considering the facts stated, it may be concluded that the product from 5N- and 6N-acid is almost entirely nitrogen trioxide (nitrous anhydride). The low values for the products in experiments 8 and 9 will be raised to the same value as the others if allowance is made for the nitrogen lost, owing to the formation of nitric oxide, this value being nearly that demanded by theory.

Allowing for the correction suggested for the products from more concentrated acid, the product from 14.5N-acid will contain 85 to 90 per cent. of peroxide, the residue being trioxide, for 10N- acid there will be about 15 to 20 per cent. of peroxide, and for the 8N-acid somewhat less.

It was not practicable to carry out work with acid more dilute than 5N, owing to the time taken for solution in a vacuum, probably on account of the continuous removal of nitrous acid, which in consequence could not exert its usual "auto-catalytic" effect.

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