XIII.—*On some Reactions of Hydriodic Acid.*

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IN a paper published in the Journal of this Society, August, 1866, "On some Decompositions of Nitrite of Amyl," I stated that the nitrite is decomposed by hydriodic acid, iodide of amyl and nitric oxide being formed; but I have since determined exactly the amount of nitric oxide liberated in this reaction, and find that it falls far short of that required on the assump-

tion that all the nitrogen is liberated in this form. $C_5H_{11}NO_2$ contains 11.966 per cent. of nitrogen, and should therefore yield 25.64 per cent. of NO. I have, as will be seen below, only been able to obtain about 18 per cent. These quantitative experiments were performed in the apparatus figured below. *b* is a stop-cock bulb-tube connected with an apparatus generating hydrogen. Its tube passes through the cork and nearly to the bottom of the flask, *c*, which contains strong hydriodic acid. *d d* is a wide tube sealed at the bottom and having a small hole at *e*. *d* is in connection with a potash apparatus containing caustic potash. This is connected with a chloride-of-calcium tube, and this again, with another potash-apparatus containing protochloride of iron. Finally, this second potash-apparatus is in connection with a small tube containing caustic potash in small lumps. To use the apparatus, it is first completely filled with hydrogen, and the strong hydriodic acid in *c* gently warmed. The stop-cock is then turned off, the tube *a* is removed from the bulb, and the bulb filled with carbonic acid. A weighed quantity of the nitrite is then introduced into the bulb, and the hydrogen-tube at once replaced. The apparatus now contains no air, so that the nitric oxide cannot be oxidized after it is once formed. The stop-cock is then turned on, and the nitrite of amyl allowed to run into the tube. It does not immediately run into the hydriodic acid, but, if the stop-cock be immediately closed, remains suspended in the tube. It is allowed to pass very slowly into the hydriodic acid, by cautiously opening the stop-cock. Nitric oxide is at once evolved and escapes through the small aperture *e*, which is now exactly on a level with the surface of the hydriodic acid, the hydrogen with which the apparatus was filled having forced the hydriodic acid, which was originally above the aperture, into the wide

tube, *d*. The gas escapes in a series of very small bubbles and is of course thoroughly washed by its ascent through the column of liquid in the tube. It passes through the potash and finally into the solution of protochloride of iron, where any nitric oxide is of course immediately absorbed. When all the nitrite has been forced into the hydriodic acid, the bulb *b* is heated, and hydrogen gas again transmitted through the liquid. In this way the last traces of nitrite are forced to pass into the hydriodic acid. The hydriodic acid itself is then heated almost to boiling, and the first set of potash-bulbs are surrounded by hot water, the stream of hydrogen being still continued for a few minutes. The chloride-of-iron bulbs with their accompanying potash tube are then detached and weighed. As they have been weighed previously, the difference in weight shows at once the amount of nitric oxide absorbed.

In one experiment (A) ·8036 of nitrite gave ·1476 of NO. Therefore 18·37 per cent. of NO. The hydriodic acid remaining in the flask was treated with excess of caustic potash and distilled into a standard solution of sulphuric acid, as it was probable that ammonia had been formed. This was found to be the case, and, from the amount of sulphuric acid neutralized, it appeared that 0·0326 of NH_3 had been produced. If we calculate from these data the total amount of nitrogen present we obtain the following results :—

From the nitric oxide	0·06888
From the ammonia	0·02684
	————
Total nitrogen found	0·09572

Therefore the total percentage of nitrogen found is 11·91. In a second experiment (B) conducted in precisely the same manner, ·9646 of nitrite furnished ·1708 of NO and ·0415 of NH_3 . We had therefore 17·706 per cent. of NO. Calculating from these results, we find,—

From the nitric oxide	0·07971
From the ammonia	0·03418
	————
	0·11389

Therefore the total percentage of nitrogen found was 11·81. The theoretical percentage of nitrite is 11·966.

That this method of estimating nitric oxide is trustworthy, I have proved by actually liberating a known quantity of nitric oxide from its solution in perchloride of iron, and estimating it in the manner described in the foregoing section. Though somewhat foreign to the subject, the details of the following experiment prove beyond all question the soundness of this statement. I mentioned in the paper already quoted, that nitrite of amyl is decomposed by sulphuric acid, valerianate of amyl, water, nitric oxide, and sulphurous acid being produced. Thus :—

I have determined the amount of protoxide liberated under these circumstances. The apparatus employed was in every respect similar to that already described, sulphuric acid being substituted for hydriodic acid. At the close of the experiment, water was added to the contents of the flask by means of the bulb-tube, thereby diluting the sulphuric acid, and liberating the nitric oxide which the concentrated acid would otherwise have retained. In order to prevent an undue rise of the acid in the wide tube *d*, the flask was tilted during and after the addition of the water. In this manner, .7962 of nitrite caused an increase of the weight of the second set of potash-bulbs of .1998. This corresponds to 25.09 per cent. of NO, or 11.71 of N, the theoretical numbers being respectively 25.64, and 11.966.

With these data before me, it appeared worth while to attempt the conversion of nitric oxide into ammonia. With this object, the nitric oxide was transmitted through boiling concentrated hydriodic acid. It was slowly absorbed, and iodine was liberated. To prevent this, a little phosphorus was added. The contents of the vessel were then poured off from the phosphorus, and excess of potash added. The smell of ammonia was immediately perceptible. It was distilled into dilute sulphuric acid, and the distillate evaporated down to a small bulk, and strong alcohol added. This at once occasioned a precipitate of sulphate of ammonium.

It appeared to me to be of interest, also, to determine the action of hydriodic acid on the *nitrates* of the alcohol radicles. This action is much less energetic than the corresponding action on the *nitrites*. The *nitrates* are not attacked in the cold by hy-

diiodic acid of sufficient strength to decompose the *nitrites* instantly. On boiling, however, the *nitrates* are pretty easily attacked, nitrate of methyl much more readily than the corresponding ethyl-compound. The products in both instances are nitric oxide, ammonia, and an iodide of the corresponding alcohol radicle.