XXXVII.—*The Formation of Hyponitrites from Nitric Oxide.*

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NITRIC oxide is slightly absorbed by a strongly alkaline solution of potassium stannite, converting it into stannate. After passing the gas for about two hours, the solution begins to effervesce slightly, especially when shaken, and continues to do so as long as the current of nitric oxide is maintained and for hours afterwards. The reaction takes place so slowly that even when our experiments lasted for two or three days, some stannite still remained unconverted to stannate.

The slowness of the change and the very slight effervescence, com-

bined with the circumstance that the nitric oxide employed is never quite pure, have prevented us from ascertaining the nature of the gaseous product of the reaction, but we believe from analogy that it is nitrous oxide. Either this or nitrogen it must certainly be. In the solution, we found a hyponitrous compound in small quantity, a very little ammonia, and traces of hydroxylamine.

Solution of potassium stannite was prepared by mixing stannous chloride solution with sodium carbonate, allowing the precipitate to subside in a closed vessel, decanting the supernatant mother-liquor as far as possible, and adding some solid potassium hydroxide to the residue. A solution was thus obtained which contained alkali chloride, and, even in the cold, deposited some black stannous oxide.

A slow and continuous stream of nitric oxide washed with alkali was passed into this solution, hydrogen being passed through the flask both before and after this treatment, in order to avoid all contact between the nitric oxide and air within the apparatus. One of two methods of treatment was now followed: either silver nitrate or barium chloride was added.

The addition of silver nitrate causes a succession of precipitates. First, there is a black precipitate produced by the unchanged stannite and by a trace of hydroxylamine; then, a white precipitate of chloride; next, a dirty grey one; and then a brown one of silver oxide. After this would come, no doubt, silver stannate, but we have not pursued the matter further, the dirty grey precipitate yielding us what we were seeking. The black precipitate which first comes down will not be produced if the solution is previously stirred with precipitated mercuric oxide, which oxidises both the remaining stannite and the trace of hydroxylamine.

The dirty grey precipitate, mixed with a little silver chloride and oxide formed before and after it, was collected apart, thoroughly washed, treated with dilute nitric acid, and the acid solution filtered and neutralised with ammonia. A bright yellow precipitate was thus obtained decomposable by hot acids, and showing the other characters of silver hyponitrite. No trace of phosphate was with it.

The addition of barium chloride to the solution which has been treated with nitric oxide, gives an amorphous white precipitate of a composite nature. If this is removed and the filtrate left to stand after addition of more barium chloride, a second crystalline precipitate slowly forms, which is converted by silver nitrate into tolerable pure silver hyponitrite. The first-formed barium precipitate after slight washing, is changed to a dirty grey-brown precipitate by silver nitrate. This when treated like that formed in the original solution by silver nitrate also yields silver hyponitrite. The total hyponitrite obtained is but small in amount, even under the most

favourably conditions of a long treatment with nitric oxide, and a nearly complete conversion of the stannite to stannate.

The reaction between the potassium stannite and the nitric oxide may be represented by the equation—

But, if we seek for a fuller insight into this reaction, we may possibly find it by taking into consideration the continual though slight effervescence which occurs in the solution, together with what happens under similar circumstances on passing nitric oxide into an alkaline solution of potassium sulphite, when much such an effervescence may also be observed. In that case nitrososulphate is formed, and in the present case it seems probable, therefore, that a *nitrosostannate* is the compound which is produced and afterwards, like the nitrososulphate, converted into hyponitrite. Its production will take place thus:—

Then the nitrosostannate must give hyponitrite with silver oxide:—

although nitrososulphates are incapable of undergoing such a change. If this explanation of what happens is correct, the dirty grey precipitate which yields hyponitrite will be silver nitrosostannate, and the effervescence will be due to the decomposition of the potassium nitrosostannate into stannate and nitrous oxide:—

a decomposition similar to that of the nitrososulphate.

According to our own experience, there are now known three distinct reactions by which hyponitrites can be formed: (1) that between amalgams of the alkali-metals and a nitrite (or nitrate); (2) that between these amalgams and a nitrososulphate; (3) and that between alkali stannites and nitric oxide in presence of free alkali afterwards acidified. According to Zorn's observations, a fourth reaction is that between ferrous hydroxide and a nitrite (or nitrate) in neutral or slightly acid solution.

Inaction of Alkali Stannites with Nitrites and Nitrates.

Neither nitrites nor nitrates undergo any change that we have succeeded in detecting, when they are treated with alkali stannite in presence of alkali hydroxide, even in hot solution. Acid solutions of stannous chloride react with nitrites and nitrates (v. Dumreicher).

Ferrous Hydroxide, and its Behaviour with Nitric Oxide, Nitrites, and Nitrates in Alkaline Solution.

Ferrous hydroxide, as commonly prepared, is a bulky, gelatinous, greenish-grey substance, exceedingly liable to oxidation, and then forming the greenish-black magnetic hydroxide which changes to red ferric hydroxide on further oxidation. If, however, after precipitation the supernatant mother-liquor is poured off and solid potassium hydroxide dissolved in the remaining mother-liquor, the ferrous hydroxide diffused through it undergoes in the course of a few hours a very considerable diminution in volume, and then forms a pale greenish-grey pulverulent precipitate, although the gelatinous precipitate may have been of a much darker colour. This dense hydroxide is much more stable, and in oxidising does not form the black hydroxide before becoming ferric hydroxide.

Such ferrous hydroxide mixed with solution of potassium hydroxide was treated for hours with nitric oxide gas. In this way the ferrous hydroxide became oxidised to ferric hydroxide, and the nitric oxide converted largely into ammonia. Neither hydroxylamine nor hyponitrite could be detected as products of this reaction.

Alkali nitrites also yielded much ammonia when treated with the mixed ferrous and potassium hydroxides, but neither hyponitrite, hydroxylamine, nor any gaseous product. Alkali nitrates were not changed in the least by the same mixture.