XIV.—*Reduction of an Alkali Nitrite by an Alkali Metal.*

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IT is already known what are the products which may result from the action of sodium amalgam on a solution of sodium nitrate or nitrite. Schonbein (1861) first observed the formation of nitrite by the action of metallic sodium on a solution of a nitrate; and de Wilde (1863) that nitrous oxide, nitrogen, and ammonia are the products of the action of sodium amalgam on a solution of potassium, sodium, or ammonium nitrate, or on potassium nitrite; he found that, except alkali hydroxide, nothing else is produced, and, in particular, no hydrogen. Some years later (1870), however, it was recognised by Fremy, aided by a suggestion of Maumené's, that hydroxylamine, or what appeared to be hydroxylamine, was a product of the reduction. Then came (1871) my own discovery of the hyponitrites, together with the observation that alkali nitrates in solution are largely convertible into nitrites by sodium amalgam, an extension of Schonbein's experience. Lastly, Haga and I (1896) proved that the actively reducing substance observed by Fremy is actually hydroxylamine, as it had been taken to be by Maumené and by him, and not hydrazine, as it might have been. By a mistake, already pointed out and corrected by me (*Annalen*, 1897, **295**, 366), the discovery of the hyponitrites has been in recent years attributed to Maumené. It will suffice here to say that this veteran French chemist has, it so happens, published, in another connection, that he had not experimentally investigated the reduction of nitrites in solution, and that, far from laying claim to the discovery of hyponitrites, he at first denied its truth on theoretical grounds (Trans., 1872, **25**, 772; *Chem. News*, **25**, 153 and 285).

Nitrous oxide, nitrogen, hydroxylamine, ammonia, sodium hyponitrite, and sodium hydroxide (from the nitrite as well as from the metal), are, according to my experience, always produced in the reduction of sodium nitrite or nitrate by sodium amalgam, but in proportions which vary greatly within well-marked limits. Nearly one-sixth of the nitrogen can be obtained as sodium hyponitrite in one way of working, or scarcely any at all in another. So, too, the range of production of hydroxylamine is from nearly 9 per cent. of the nitrogen of the nitrite down to one-third per cent. The presence of ammonia may be very strongly manifest, or be hardly perceptible and escape notice. The two gases, nitrous oxide and nitrogen, together represent at least 80 per cent. of the total nitrogen, and may vary in relative proportion to the extent of either of them being nearly absent. Necessarily, all the sodium of the nitrate or nitrite, not left as hyponitrite, appears as hydroxide, along with that derived from the metallic sodium used as the reducing agent. So long as any nitrite remains, hydrogen does not occur among the products, unless a very large quantity of water is present, whilst, if there is very little water, hydrogen is not evolved even after all the nitrite is gone.

Within the limits indicated, the proportioning of the products of the reduction is well under control. The concentration of the solution of nitrite, or, to put it better, the relative quantity of water present, exercises most influence, the only other circumstance affecting the course of the reduction being the temperature. The concentration of the sodium in the amalgam and the proportions of the sodium and the nitrite have no direct effect on the reduction. Working with a sufficiently concentrated solution of nitrite, the proportions of the products remain constant throughout the reduction of the nitrite. Probably this is the case also when an exceedingly dilute solution is used; but with a somewhat dilute solution, say 1 in 30, there is some difference, due to the fact that the presence or absence of much sodium hydroxide modifies the proportions of the products, and that this substance is generated so largely. A dilute solution of sodium nitrite may be made to behave as a concentrated solution in the mode of its reduction by nearly saturating it with sodium hydroxide before bringing it in contact with the sodium amalgam; but the addition of sodium hydroxide to a concentrated solution of nitrite before reducing it by the amalgam has no sensible effect, for the reason, no doubt, that, in the reduction of the nitrite as it actually occurs, about $3\frac{1}{2}$ mols. of sodium hydroxide are produced for 1 mol. of nitrite reduced, quite enough, therefore, of itself to make the water of a concentrated solution almost proof against the action of sodium. With a large quantity of water present, the sodium hydroxide formed is not enough to render the water inactive, and in this is to be found the explanation of the great difference observed in the proportions of the products, according as the nitrite is dissolved in much or little water.

In order to produce as much *hyponitrite* as possible, little more is necessary than to work with a concentrated solution of the nitrite (1 of sodium nitrite to 3 or 3½ water), to add the amalgam in some excess, and not to allow the temperature to rise above 100°. To get as much *hydroxylamine* as possible, the solution of nitrite must be dilute (say 1 in 50), and be kept cold during the addition of the amalgam. To preserve the hydroxylamine from reduction to ammonia, the solution must be kept well agitated over the amalgam, and be poured off from it as soon as nearly all the nitrite has been reduced. Much more time is needed to reduce a dilute solution than a concentrated one. The best conditions for producing much hydroxylamine do not allow of much more than half the maximum yield of hyponitrite being obtained at the same time.

To get much *nitrous oxide*, the temperature of the solution must be kept as low as possible, whilst to get much *nitrogen*, the temperature must be kept high, the strength of the solution of nitrite being without effect. The reduction of a very dilute solution of sodium nitrite kept very cold is attended with very little effervescence, because the quantity of nitrogen produced is very small and the nitrous oxide remains dissolved, although it is readily evolved on warming. De Wilde has determined the proportions of the gases to each other, but only when the nitrite (or nitrate) was in excess of the sodium ; that however, is sufficient, since qualitative examination of the gases has shown me that variations in the proportions of salt and metal are without sensible influence on the composition of the gases, and also that this remains apparently unchanged during the progress of the reduction if the temperature is kept tolerably uniform. De Wilde found that dilute solutions of nitrite or nitrate of sodium or potassium gave larger quantities of nitrous oxide in proportion to nitrogen when the solutions were dilute than when they were concentrated, from which it might seem that the strength of the solution does affect the proportions of the gases to each other; but in the experiments conducted by de Wilde, the much greater rise of temperature when concentrated solutions are acted on fully accounts for the results he obtained.

Ammonia can always be detected from the beginning of the reduction (Thum thought not), but its amount may be minute throughout. It can be got in considerable quantity by using a cold dilute solution, as for producing hydroxylamine, and, after the main action is over, shaking it with amalgam in a stoppered bottle until all the hydroxylamine has disappeared. It can also be got somewhat concentrated for a short time by dropping the concentrated solution of the nitrite on to much solid sodium amalgam, as was first observed by de Wilde but even then much hyponitrite is produced. Very hot and dilute solutions of nitrite treated with sodium amalgam give little else than ammonia and nitrogen.

The reduction of potassium nitrite by potassium amalgam closely resembles that of the sodium salt by sodium amalgam, in every respect, both quantitative and qualitative.

If, for the moment, nitrogen and hydroxylamine be disregarded, as they well may be, since their proportions become very small under suitable circumstances, the nitrite may then be said to be reduced simply to hyponitrite and much of this hydrolysed into nitrous oxide and sodium hydroxide. This, at one time, I, as well as other chemists, supposed to be the case. But, for a long time now, I have felt that most of the nitrous oxide and sodium hydroxide must have another origin. Thum has expressed himself in the same sense, basing his opinion upon the comparative stability of sodium hyponitrite in strongly alkaline solution, for it is only gradually decomposed even when boiled with it. This fact by itself, however, is not inconsistent with the assumption that the nitrous oxide and sodium hydroxide represent decomposed hyponitrite. But it does not stand alone; for (*a*) Hot concentrated solutions of nitrite yield quite as much hyponitrite as cold ones, unless the temperature is well above 100°, and even then the yield does not fall off much. (*b*) In all cases, the effervescence accompanying the formation of hyponitrite goes on exclusively at the surface of contact with the amalgam. (*c*) Low production of hyponitrite is not attended with higher production of nitrous oxide. All these facts are opposed to the view that the nitrite is all reduced to hyponitrite in the first place; so, too, is what follows.

Although the proportions of the products of the reduction of the nitrite vary greatly with the circumstances, it is only within well-marked limits; thus, of the nitrite reduced there is from a sixth, under one set of conditions, to almost a fifth, under other conditions, which becomes partly hyponitrite and partly hydroxylamine (and ammonia), whilst the rest becomes nitrogen and nitrous oxide, one or the other predominating, according to circumstances. So, too, in one extreme case, nearly all of the one-sixth of the nitrite will change into hyponitrite, very little becoming hydroxylamine; or, on the other hand, of nearly one-fifth of the nitrite more than half may be converted into hydroxylamine, only the rest of the fifth becoming hyponitrite. It may, therefore, safely be assumed that about one-fifth of the nitrite tends to, or is able to, become hyponitrite, although barely one-sixth of the nitrate can yet be secured as this salt, because either some of this fifth becomes hydroxylamine, or else a little of the hyponitrite is hydrolysed at once or during the process of isolating it. With that assumption to give more precision to the statement, it may be affirmed that many experiments under varied conditions have shown that about a fifth of the nitrite is decomposed by sodium amalgam in one way, and four-fifths in another way; in the one, hyponitrite, hydroxylamine, and alkali (with a very little ammonia and nitrous oxide as secondary products) are formed, and in the other, nitrogen, nitrous oxide, and alkali; so that when much hydroxylamine is formed it is at the expense of hyponitrite only, and when much nitrogen is produced it is at the expense of the nitrous oxide only.

But although this is the case, the hydroxylamine does not seem to be derived from the hyponitrite, or the nitrogen from the nitrous oxide, but, rather, the one pair of substances is derived from one transition product, and the other pair from another transition product. It was pointed out in my first paper that sodium amalgam does not act on hyponitrite, and this has since been more fully established by Dunstan and Dymond, and again by Thum; according to the last-named chemist, hyponitrous acid is not reduced even by zinc and boiling dilute sulphuric acid. In confirmation of my earlier statement, I can now assert that sodium amalgam has no action whatever on a solution of sodium hyponitrite saturated with sodium hydroxide, even at 80° (and, no doubt, at higher temperatures), and when in contact with it for days together; no hydroxylamine, ammonia, nitrogen, or hydrogen is produced. In weaker alkaline solutions, hydrogen is very slowly evolved, but still without the hyponitrite being affected. Weak alkaline solutions of sodium hyponitrite, however, slowly decompose of themselves, and then some of the nitrous oxide may possibly get reduced by the sodium amalgam.

As for the nitrogen, it is evident that only while nitrous oxide remains in solution and comes in contact with the amalgam can it be reduced, even if it is then (see p. 95). Yet, in order to get much nitrogen in place of nitrous oxide, it is necessary to work with hot solutions, when the solubility of nitrous oxide is at its lowest. It is not essential that the quantity of nitrite should be small in proportion to the sodium, temperature alone appears to be the condition determining the formation of nitrogen in place of nitrous oxide. In other words, weak solutions of nitrite and excess of amalgam in no degree favour the production of nitrogen rather than of nitrous oxide, and the proportion of nitrogen is not greater in the gases escaping towards the end of a reduction than at the beginning.

Very different is it with ammonia, which is truly a product of the reduction of hydroxylamine (in non-acid solution), and the formation of which takes place principally during the final action of the amalgam. Against the notion, highly improbable as it is, that the nitrogen may come from yet undecomposed nitrite and already formed ammonia, which would also account for the comparative absence of ammonia in the earlier part of the reduction, there may be adduced de Wilde's observation, that ammonium nitrate, when reduced by sodium amalgam, gives much more nitrous oxide in proportion to nitrogen than potassium or sodium nitrate does, no doubt because there is less rise in temperature.

Without speculating on the constitution of a nitrite, we are able to see from the interactions between ethylic iodide and silver nitrite that a nitrite may react both as an oxylic salt, NaONO, and as a halide, $NaNO_2$. From the reduction by sodium there will then first result the radicles NaON= and NaNO; from the former, or sodoximido-radicle, may well come the hyponitrite and hydroxylamine, and from the other, or sodium nitroside radicle, the nitrous oxide and nitrogen. In accordance with the facts observed, the sodoximide, in concentrated alkaline solution, will condense to sodium hyponitrite, stable against reduction, or, in very dilute alkaline solution, will, by hydrolysis and reduction, become alkali and hydroxylamine. The hypothetical nitroside will also condense and simply hydrolyse into nitrous oxide and alkali, mainly at low temperatures, or will become reduced and hydrolysed into nitrogen and alkali, principally at higher temperatures.

To establish the points in the reduction of the two nitrites by their respective metals, here described, I have made very many experiments, usually working on quarter-gram molecules of nitrite. The hyponitrite obtained was weighed as silver salt. The hydroxylamine was estimated by the quantity of metallic silver it yielded, and in this way: the black precipitate it causes in silver nitrate solution, in presence of alkali, being largely suboxide, was washed with cold dilute nitric acid and ammonia alternately, and the residual brownish metallic silver weighed and calculated into hydroxylamine by the ratio $2Ag : NH_3O$, experiments (described in the next paragraph) with solution of hydroxylamine sulphate of similar dilution and alkalinity having shown that this could be done accurately enough.

The important observation, made by Thum, that hydroxylamine, when oxidised by suitably alkalised mercuric oxide, silver oxide, or cupric hydroxide, will yield a little hyponitrite and nitrite, induced me to ascertain whether, in my experiments, the destruction of hydroxylamine in this way, sometimes in considerable quantity, might not account for some of the hyponitrite afterwards found to be present. To ascertain whether this took place, I made a blank experiment very similar to those made in studying the reduction of sodium nitrite, except that sodium hyponitrite itself was absent. Thus, hydroxylamine sulphate, 1·5 grams (= 0·6 gram hydroxylamine) was dissolved along with 32 grams of sodium hydroxide in nearly 2 litres of water, and then a solution was run in, with stirring, of 7·5 grams of silver nitrate, which was a considerable excess, such as was used in the other experiments. The abundant, black precipitate was washed, exhausted with ice cold, dilute nitric acid, and the solution, neutralised as usual in my other experiments, gave no silver reaction for silver hyponitrite, and nothing more than a slow and very slight action on permanganic acid, which might be due to a trace of either nitrous or hyponitrous acid. It was easily seen that some nitrous acid was formed, by applying the iodide and starch test. Under the circumstances of my experiments, therefore, even when 7 per cent. of the nitrite had been reduced to hydroxylamine, there could have been no perceptible production of hyponitrite during the after oxidation of the hydroxylamine. The metallic silver, washed out with dilute nitric acid * and ammonia, weighed 3·8 grams, the calculated quantity being 3·95 grams. The nitrite detected in the mother liquor of the black precipitate had been formed in too small a quantity to materially affect the weight of the metallic silver.

Generally, sodium hydroxide was approximately estimated, after all the hyponitrite had been precipitated, by titration of the mother liquor with nitric acid, and of the silver oxide that had been precipitated along with the silver hyponitrite and the metallic silver. The amalgam used was of approximately known strength, ascertained, not by sampling, which is impracticable, but by uniformly preparing successive quantities, and sacrificing one to assay by dilute sulphuric acid and weighing the sodium as sulphate; after use in reducing nitrite, the sodium remaining in the mercury was sometimes determined in the same way. Nitrous oxide and nitrogen were not measured; their total nitrogen was found by difference, and their proportions had been sufficiently ascertained by de Wilde, as I have already said; but their relative abundance was estimated by a burning splint of wood, the reduction of the nitrite being always conducted in a loosely closed flask. The range of this reaction was from that of a gas utterly extinguishing combustion to that of one which supported it most vividly; in any uniformly conducted experiment, the gases evolved towards the end behaved like those given off at first.

To ascertain the effect on its reduction by sodium of adding sodium

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* It was proved many years ago that silver is insoluble in dilute nitric acid, the presence of nitrous acid being necessary to make it dissolve. But the contrary has been since asserted to be true where the silver is finely divided, as when precipitated. This error, as I must regard it, is due to precipitated silver when black or blackish containing suboxide, which gives it its colour: this is resolved by acids into oxide of silver, which dissolves, and metallic silver, which is left.

hydroxide to a concentrated solution of sodium nitrite (negative as this proved to be), two methods were adopted. In one, the amalgam was covered with a cold saturated solution of sodium hydroxide, which has no action on it, and then the concentrated solution of nitrite was slowly added; at first, the alkali greatly impedes the action of the amalgam on the nitrite, but when more of the solution of the latter is added, the action goes on faster and to the end, and gives the usual large proportion of hyponitrite with very little hydroxylamine. In the other, a concentrated solution of sodium nitrite and sodium hydroxide was treated with some of the amalgam; then more sodium nitrite was added, and then more amalgam. The result was the same as before. The object of working in this way was to obtain the effect, if any, of the most concentrated alkali from the first, without having to deal afterwards with a very large excess of alkali when the analysis had to be made.

I have also tried to ascertain the effect of diminishing the amount of alkali present. In acid reducing mixtures, nitrous acid becomes largely converted into hydroxylamine without production of hyponitrous acid, so that it seems probable that, could the alkali formed in the reduction of the nitrite by sodium be neutralised nearly as fast as it is produced, much hydroxylamine would be obtained and very little hyponitrite. The use of the ordinary acids for the purpose in such a way as to give conclusive evidence on the point does not seem to be practicable, whilst the great rapidity of the process of reduction makes the use of carbon dioxide (Aschan, *Ber.*, 1891, **24**, 1865) very unpromising. I have, therefore, tried the effect of adding ammonium acid carbonate along with the sodium nitrite, expecting the ammonia to be inactive. In one case, where I used the amalgam in large excess, much ammonium amalgam was formed, and, what was quite unexpected, neither hyponitrite nor hydroxylamine. In another experiment, in which the nitrite was kept in excess of the amalgam, the previous addition of the ammonium carbonate in excess was without any effect; the nitrite solution had to be used slightly dilute because of the carbonate, and gave, therefore, a little less hyponitrite (about 12·7 per cent. of the nitrite consumed) and a little more hydroxylamine (about 3 per cent.) than in the best way of working for hyponitrite. The presence of the ammonium carbonate was, therefore, without effect, the reaction between the nitrite and the sodium being already complete when the sodium oxide comes in contact with the water and ammonium carbonate.

I satisfied myself that a fairly concentrated solution of nitrite is uniformly reduced from the commencement to the end of the reaction if the temperature is kept tolerably constant, the method employed being to examine the gases in the way described, and the hyponitrite and hydroxylamine as follows. To a solution of nitrite, one-half only of the quantity of sodium amalgam required to reduce it was added, and it was then found to contain hyponitrite and hydroxylamine in the same relative proportion as if the nitrite had been fully reduced (with cooling), and in approximately half the quantities the nitrite would have yielded if the full amount of sodium amalgam had been added.

Sodium amalgam was proved to have little or no action on nitrous oxide by exposing the gas for a long time to its action. The amalgam was liquid, and, when shaken up with the moist nitrous oxide in a stoppered bottle, coated the sides of the bottle. With occasional vigorous shaking, the bottle was kept closed four days; when opened, it was found to contain the nitrous oxide little, if at all, deteriorated as a supporter of combustion. In another similar experiment, a saturated solution of sodium hydroxide was poured over the amalgam; in this case, the amalgam did not coat the sides of the bottle, but the solution served to keep the dissolved nitrous oxide in contact with the amalgam. The bottle was often vigorously shaken, and was not opened until after four days. The nitrous oxide was almost or quite unchanged. Holt and Sims have studied the oxidation of sodium and potassium by nitrous oxide, but only at much higher temperatures than those in these experiments, which were at 25—30°.

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