

## The Reduction of an Alkali Nitrite by an Alkali Metal.

By

Edward Divers, M. D., D. Sc., F. R. S., Prof.,  
Imperial University, Tokyo.

What the products are which may result from the action of sodium amalgam upon solution of sodium nitrate or nitrite is already known. Schoenbein (1861) first observed the formation of nitrite by the action of metallic sodium upon solution of a nitrate; and de Wilde (1863) that nitrous oxide, nitrogen, and ammonia are the products of the action of sodium amalgam upon a solution of nitrate of potassium, sodium, or ammonium, or upon one of nitrite of potassium. He found that, except alkali hydroxide, nothing else is produced and in particular no hydrogen. But, some years after (1870), it was recognised by Fremy, aided by a suggestion of Maumené's, that hydroxylamine, or what appeared to be it, 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 Schoenbein'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 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. (*J. Ch. Soc.*, 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 the substances always all produced, according to my experience, in the reduction of sodium nitrite or nitrate by sodium amalgam, but in proportions which greatly vary 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 a 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 between themselves to the extent of either of them being nearly absent. Necessarily all the sodium 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, no hydrogen appears among the products, unless a very large quantity of water is present, while when there is exceedingly little water hydrogen is not formed even after all nitrite is gone.

Within the limits indicated, the proportioning of the products of the reduction is well under control. The concentra-

tion 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 is the temperature at which it is allowed to proceed. The concentration of the sodium in the amalgam and the proportions of the sodium and the nitrite are without 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 of nitrite is used, but with a somewhat dilute solution, say one in 30, there is some difference, due to the facts that the presence or absence of much sodium hydroxide modifies the proportion 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. The addition of sodium hydroxide to a concentrated solution of nitrite before reducing it by sodium amalgam has no sensible effect, for the reason, no doubt, that in the reduction of the nitrite, as it actually occurs, about  $3\frac{1}{2}$  mol. sodium hydroxide are produced for one mol. 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 sodium nitrite to 3 or  $3\frac{1}{2}$  water), and add the amalgam in some excess. All else to attend to is that the temperature should not be allowed to rise above  $100^{\circ}$ , at first, as the yield is a little lowered otherwise. 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 into ammonia, the solution should throughout be kept well agitated over the amalgam and be poured off from it as soon as nearly all nitrite has been reduced. Much more time is needed to reduce a dilute solution than a concentrated one. The best conditions for producing hydroxylamine, do not allow of much more than half the best 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, while to get much *nitrogen* the temperature must be kept high. The strength of the solution of nitrite is here without effect, provided that the temperature is properly regulated by external heating or cooling, as may be called for. 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, though ready to escape when the solution is warmed. De Wilde has determined the proportions of 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 upon the composition of the gases, and also that this remains apparently unchanged during the progress

of a reduction when 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 strength of 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 upon 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 hydroxylamine has disappeared. It can also be got somewhat concentrated for a short time by dropping the concentrated solution of the nitrite upon much solid sodium amalgam, as was first observed by de Wilde; but even then much hyponitrite is still 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 is closely like that of the sodium salt by sodium amalgam, in all respects, quantitatively as well as qualitatively.

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 to be hydrolysed into nitrous oxide and sodium hydroxide. This at one time I supposed to be the case, and other chemists

have done the same. 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, in which it can be boiled with only gradual decomposition. This fact by itself, however, is not quite inconsistent with the assumption that the nitrous oxide and sodium hydroxide represent decomposed hyponitrite. But it does not stand alone; there are other facts which tell greatly against the probability of hyponitrite being the source of most of the nitrous oxide obtainable by the reduction of nitrite. (a) Hot concentrated solutions of nitrite yield quite as much hyponitrite as cold ones, unless the temperature is well above  $100^{\circ}$ , 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.

The proportions of the products of the reduction of the nitrite vary greatly with the circumstances, but yet 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); while the rest becomes nitrogen and nitrous oxide, one or the other predominating, even largely, 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, of nearly one-fifth of the nitrite more than half may be converted into hydroxylamine, only the rest of the fifth becoming hyponitrite, in the other extreme case. 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 nitrite can yet be secured as this salt, because either some of this fifth becomes hydroxylamine instead, or, else, that a little 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 one are formed hyponitrite, hydroxylamine, and alkali (with a very little ammonia and nitrous oxide as secondary products), and in the other way, nitrogen, nitrous oxide, and alkali : so that when much hydroxylamine is got it is at the expense of hyponitrite only, and when much nitrogen is got it proves to be at the expense of the nitrous oxide only.

But though this is the case, there seems to be no derivation of the hydroxylamine from the hyponitrite, or of the nitrogen from the nitrous oxide, but, rather, the derivation of the one pair of substances from one transition product and of the other pair from another transition product. It was pointed out in my first paper that sodium amalgam is inactive upon 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 even reduced by zinc and boiling dilute sulphuric acid. I can now assert, in confirmation of my earlier statement, that sodium amalgam has

no action whatever upon a solution of sodium hyponitrite saturated with sodium hydroxide, even when heated to 80° (and no doubt higher), and for days together; no hydroxylamine, ammonia, nitrogen, or hydrogen is produced. In weaker alkaline solutions, hydrogen is very slowly produced, but still without any effect upon the hyponitrite. Weakly alkaline solutions of sodium hyponitrite slowly decompose of themselves, and then some of the nitrous oxide may possibly get reduced by the sodium amalgam, (see p. 31).

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. 31). 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 nitrite should be in small proportion to the sodium, temperature alone appears to be the condition determining the replacement of nitrous oxide by nitrogen. 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 nitrogen does not prevail more in the gases escaping near the end of a reduction than near its beginning.

Very different is it with ammonia, truly a product of reduction of hydroxylamine (in non-acid solution), 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 existent 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 does potassium or sodium nitrate (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 ethyl iodide and silver nitrite that a nitrite may react both as an oxylic salt  $\text{NaONO}$  and as a halide  $\text{NaNO}_2$ . From the sodium reduction there will then first result the radicals  $\text{NaON=}$  and  $\text{NaNO}$ . From the former or sodioximido radical may well come the hyponitrite and hydroxylamine, and from the other or sodium nitrosyl radical the nitrous oxide and nitrogen. In accordance with the facts observed, the sodioximide, in concentrated alkaline solution, will condense into 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, principally 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 upon 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, this was washed out with cold dilute nitric acid and ammonia alternately, and the residual brownish metallic

silver weighed and calculated into hydroxylamine by the ratio  $2\text{Ag}:\text{NH}_3\text{O}$ , experiments (described in the next paragraph) with solution of hydroxylamine sulphate of similar dilution and alkalinity having shown me that this could be done correctly enough.

The important observation made by Thum, that hydroxylamine when oxidised by suitably alkalisied mercuric oxide, silver oxide, or cupric hydroxide, will yield a little hyponitrite, and nitrite, caused me to ascertain whether in my experiments the destruction of sometimes much hydroxylamine in this way might not contribute some of the hyponitrite afterwards found present. To this end I made a blank experiment, closely 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 sodium hydroxide in nearly 2 litres of water and then a solution was run in with stirring, of silver nitrate 7.5 grams, which constituted a good excess, such as was used in the other experiments. The abundant black precipitate was washed and exhausted with ice-cold dilute nitric acid. This 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 upon 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 will 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 hyponitrite had been precipitated, by titration with nitric acid of the mother-liquor and the silver oxide precipitated with the silver hyponitrite and 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 sodium as sulphate. After use in reducing nitrite, the sodium remaining in the mercury was sometimes similarly determined. 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 at first given off.

To ascertain the effect upon its reduction by sodium, nega-

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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 to be) is due to precipitated silver when black or blackish containing suboxide, which gives it its colour: this is resolved by acid into oxide of silver which dissolves, metallic silver remaining.

tive as this proved to be, of adding sodium hydroxide to a concentrated solution of sodium nitrite I proceeded in two ways. In one the amalgam was covered with a cold saturated solution of sodium hydroxide, which is quite inactive upon it; then the concentrated solution of nitrite was slowly added. At first, the alkali greatly impedes the action of the amalgam upon the nitrite but with more of the solution of the latter added the action goes on faster and to the end and gives the usual large proportion of hyponitrite and very little hydroxylamine. In the other way of testing the point, some concentrated solution of sodium nitrite and sodium hydroxide was treated with some amalgam; then more sodium nitrite was added and then more amalgam. The result was the same as before. My aim in thus working was to have the effects, if any, of the most concentrated alkali from the first, without having to deal afterwards with too inordinate an excess of alkali, when the analysis had to be made.

I have also tried to ascertain the effect of lessening 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 reduction of nitrite by sodium be neutralised nearly as fast as produced, much hydroxylamine would be got 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, while 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 I used the amalgam in large excess, which soon gave me much ammonium amalgam, and what was quite unexpected neither hyponitrite nor hydroxylamine. In another experiment in which I kept the nitrite in excess of the amalgam, the previous addition of the ammonium carbonate in excess was without 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 presents itself to the water and ammonium carbonate.

I satisfied myself that a fairly concentrated solution of nitrite is uniformly reduced from beginning to finish, the temperature being preserved tolerably constant, by the simple examination of the gases in the way described and by the following device as regards the hyponitrite and hydroxylamine. A given solution of nitrite received with cooling only half the quantity of sodium amalgam sufficient to reduce it, and was then found to contain hyponitrite and hydroxylamine in the same proportions to each other as if the nitrite had been fully reduced (with cooling) and in tolerably nearly half the quantities the whole nitrite would have yielded.

Sodium amalgam was proved to have little or no action upon 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 nitrous oxide dissolved in contact with the amalgam. The bottle was often vigorously shaken and was not opened till after four days. The nitrous oxide remained almost or quite unchanged. Holt and Sims (*J. Ch. Soc.*, 1894, **65**, 432) have studied the oxidation of sodium and potassium by nitrous oxide, but only at much higher temperatures than those in these experiments, which were 25–30° (hot weather).

