XIII.—On Hyponitrites.

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THE hyponitrites were discovered by one of us in 1871, and briefly described by him in a paper which appeared in the *Proceedings of the Royal Society* of that year.* In 1877, Zorn issued the first of a series of communications on the same subject which has been continued by him nearly up to the present time (*Ber.*, **10**, 1306; **11**, 1630 and 2217; **12**, 1509; **15**, 1007 and 1258). Closely following Zorn's first paper, came one from van-der-Plaats (*Ber.*, **10**, 1507), and in the next year another by Menke (*Chem. Soc. J.*, Trans., **33**, 401). Lastly, Berthelot and Ogier (*Compt. rend.*, **96**, 30 and 84; *Chem. Soc. J.*, 1883, Abstr., 422) have recently published, in two parts, a paper on the silver salt.

The authors of the present note have been together engaged for some time, in spare moments, on the investigation of hyponitrites, and although they have, as yet, but little actually new to make known, they are led to publish without further delay part of what they have done, by the statements occurring in the papers of other workers on the subject, and more especially by the important ones made by Berthelot and Ogier. These papers, besides containing additions to the knowledge of hyponitrites, go over most of the work already done by one of us, and give results which sometimes confirm, but sometimes conflict with, his statements.

Composition of Silver Hyponitrite.

One of us has given the composition of the silver salt as being silver, nitrogen, and oxygen in the proportions of 1 atom of each. When he published this statement, the evidence in support of it was such as to leave no doubt in his mind as to its accuracy, although he had then only made determinations of the silver, and obtained quantities

* *Note by Edward Divers.*—It may have been supposed, from my silence upon the subject of the hyponitrites for a number of years, that I had ceased to be much interested in them, or to recognise the obligation that I was under to proceed with their investigation. Such, however, has not really been the case, and only unavoidable circumstances—more especially other active occupations—have prevented me from bringing any part of the investigation to a state fit for publication. I have now the benefit of the co-operation of my former pupil, Mr. Haga, and if I can retain this, I hope that some progress will from this time be made in the investigation, although it may still not be very rapid.

which were not closely concordant, and moreover about 1 per cent. too low. He stated that the salt slightly decomposed when it was heated to expel traces of moisture, and contained in consequence, sometimes when prepared for analysis, traces of brown or black matter, and he suggested that the silver was too low through the presence of moisture and other impurities. This explanation of the deficiency of the silver was not indeed very satisfactory, but his assertion that there could be no doubt as to the composition of the salt was justified, we think, by considerations such as the following, even at that time when other facts were wanting in support of it.

No other element had been found in it, but a minute trace of hydrogen sufficient to form water with only a very small fraction of the oxygen. It appeared to be a well-defined substance which could be repeatedly redissolved and reprecipitated without changing its properties. The amounts of silver found approached the calculated quantity closely, and yet varied among themselves so as to suggest the presence of impurity in the several portions analysed, probably in the form of products of decomposition. Evidence that such impurities were present was not wanting. The salt could not be represented as

mixture of two substances of simple composition without assuming one to be present in small quantity only. Another formula could not be taken for it that would not be at least as complex and improbable as the one recently adopted by Berthelot and Ogier of $\text{Ag}_4\text{N}_4\text{O}_6$. Its mode of formation and the main facts of its decomposition pointed to the composition given to it. Lastly, its constitution as hyponitrite was the one in accordance with the simple constitution of other oxygen-nitrogen salts.

These considerations, which still hold good, and which we offer in justification of the inference then made, it might be deemed unnecessary here to detail, because the correctness of this inference has been fully affirmed by Zorn, by van-der-Plaats, and by Menke, who have all published their success in preparing the salt pure for analysis, apparently without difficulty and without taking special precautions—this success leaving no longer any need for the inference. But it can hardly be looked upon as unnecessary, now that Berthelot and Ogier have asserted that the amount of silver in the hyponitrite is not quite the lowest even which one of us had found it to be, and less therefore than that required by the formula AgNO , and that Zorn, Van-der-Plaats, and Menke could not have got a salt answering in composition to this formula, and only through its decomposition by the heat they all employed could they have got the required percentage of silver.

Very many careful experiments of our own confirm the accuracy of this statement of Berthelot and Ogier. Before, indeed, their paper

was published, we had learned that without decomposition it seemed to be impossible to obtain, by the method of preparation employed by all of us in common, higher numbers for the silver than the lowest published by one of us.

This circumstance did not, however, lead us to doubt for a moment that the hyponitrite had the simple composition attributed to it, and it was to us a matter of astonishment to see Berthelot and Ogier giving a new formula based upon only the evidence they adduced. They indeed admit hesitation in proposing their new formula, but find reason for so doing in the results of their investigation of the quantitative reactions of the salt. We proceed to summarise their paper so far as is necessary.

They prepared the salt and purified it by dissolution in nitric acid and reprecipitation with ammonia, as one of us directs, and dried the washed salt *in vacuo* at ordinary temperatures in the dark. Thus they obtained a preparation free from any reduced silver, but containing some water. We frame the subjoined table of their results and calculations:—

	Found.						Calculated.	
	Omitting water.						$\text{Ag}_4\text{N}_4\text{O}_5$.	AgNO_3 .
	(a)	(b)	(c)	(a)	(b)			
Silver	75.3	75.0	75.3	76.2	76.1	76.1	78.3	
Nitrogen.....	9.6	9.6	—	9.7	9.8	9.9	10.1	
Water.....	1.1	1.5	—	—	—	—	—	
Oxygen by diff.	14.0	13.9	—	14.1	14.1	14.0	11.6	

They mention also a percentage of 75.5 silver. They regard the water as non-essential, and give the salt the formula $\text{Ag}_4\text{N}_4\text{O}_5$, which, as will be seen, agrees most closely with their analyses. Not contenting themselves with these, they took the pains to verify the correctness of the above ratios of the elements by quantitative estimations of the products of the decomposition of the salt by heat, by dilute sulphuric acid, and by bromine. Some of the results they thus gained we expect to discuss in a future communication.

The remarkable thing to us about their investigation is that they should not have been induced by some consideration of the strange constitution such an acid as $\text{H}_4\text{N}_4\text{O}_5$ must have, and of the probability that they might be dealing with a mixture of hyponitrite with nitrite or nitrate, to test the effect upon their preparations of some variation in the method of purification. For there is nothing to be found in the results of their extended examination of the reactions of the substance in their hands, that is not quite consistent with the assumption of its having been a mixture of hyponitrite with nitrite or

nitrate, excepting perhaps the insolubility, apparent or real, of such a salt if present. However, they seem to have felt no need for such testing, and from their paper it stands uncertain whether they even worked with more than one preparation in their three direct analyses.

For ourselves, with the facts before us that the hyponitrites would, as products of the action of sodium, not improbably be readily oxidisable; that nitrites, including silver nitrite (Divers), undergo atmospheric oxidation; and that our preparations varied in composition, we felt that our task should be to endeavour to purify the hyponitrite from firmly adhering nitrite or nitrate, or to protect the salt from oxidation during drying, or to do both these things, and in all cases to be specially on our guard against any decomposition by heat.

The results we have obtained in this work deprive Berthelot and Ogier's formula of all claim to be accepted before any other that might be devised to express the composition of some mixture of hyponitrite with nitrite or nitrate, obtainable with tolerable uniformity by some special routine in preparing it. They also show that hyponitrite very nearly if not quite pure, can be prepared. We now give an account of some of our experiments.

The silver hyponitrite we analysed was prepared in comparatively small quantities at a time, and was preserved under water in the dark, after undergoing a first purification by one or more repetitions of dissolution in nitric acid, and reprecipitation by ammonia or sodium carbonate. For each analysis a portion was submitted to a separate and further treatment with nitric acid and sodium carbonate.* Except where mentioned, the hyponitrite was washed with acetic acid to remove any silver carbonate that might be present. A valuable property of sodium carbonate for our purpose was that of decomposing silver nitrate and nitrite without having any action upon hyponitrites.

I. Washed on a filter and dried on it, in the dark, over sulphuric acid in a vacuum, without heat, 0.4734 gram of hyponitrite, dissolved in nitric acid and decomposed by hydrochloric acid, gave 76.58 per cent. silver.

II. Treated in the same way, 0.5483 gram gave 76.73 per cent. silver.

* We replaced the use of ammonia for reprecipitating from nitric acid, originally employed by one of us and afterwards by others, by that of sodium carbonate, for one reason because we noticed a paleness in colour of some of our precipitates, which appeared to be due to the ammonia combining to some extent with the hyponitrite, but we are by no means certain that this precaution—any more than some others, such as the screening from light—was really needed.

III. Not liking the paper-filter because it blackened a little, and necessitated the selection of yellow salt from discoloured portions, and further drying in a watch-glass, we no longer used it, but this time tried an asbestos filter. We also dried the salt in this case, and all others after it, in a tube connected with a Sprengel pump, and holding much sulphuric acid, which we will presently describe more fully. In this analysis 0.3369 gram hyponitrite gave 76.54 per cent. silver.

IV. The drying was effected this time in a capsule placed in a desiccator, and then in a tube connected with the Sprengel pump. Hyponitrite, 0.2760 gram, gave 76.19 per cent. silver. In these four determinations of silver, as well as in all those which follow, the salt dissolved after drying, in both nitric acid and ammonia, without leaving a trace of insoluble matter.

We had thus in the above-described experiments obtained more than 1 per cent. silver higher than Berthelot and Ogier had got, by a proceeding almost identical with that followed by them, and no more open to objection than theirs.

Berthelot and Ogier ..	75.3	75.0	75.3	75.5
Divers and Haga	76.58	76.73	76.54	76.19

Their preparations, however, contained more than 1 per cent. of water, whereas ours, we believe, were nearly, if not quite free from water. By allowing for this water they calculated their silver to be (see table already given) 76.2 and 76.1 per cent.; about half a per cent., that is, less than ours. Any way regarded, here is an excess of silver found by us that is inconsistent with the formula $\text{Ag}_4\text{N}_2\text{O}_5$, requiring as this does 76.1 per cent.

The difference between their results and ours being readily explicable on the supposition that our preparations contained less nitrite or nitrate than theirs, we tried to get other percentages of silver by variations in preparing the salt for analysis. We had observed that silver hyponitrite did not always possess even the slight solubility in water sufficient to cause an opalescence with hydrochloric acid on standing, which one of us had described it to have, it being sometimes in fact practically insoluble in water. We were thus led to suppose that its apparent slight solubility at other times might be due to oxidation. Indications of the presence of nitrite and nitrate were to be found in the wash-water, even after protracted washing, but then this might be only some obstinately adhering and slowly washing out. Water deprived of air by boiling showed, however, a distinctly less solvent power than other water, and it therefore became tolerably certain that atmospheric oxidation of the hyponitrite did occur. The

next two experiments were consequently instituted to settle the point.

In two experiments purified hyponitrite was left for about fifteen days or so with water in a covered basin in the dark, or until the water had almost dried up. The drying was then finished in the Sprengel vacuum for two days by the side of sulphuric acid.

V. 0.1188 gram gave 75.63 per cent. silver.

VI. 0.2305 gram gave 75.82 per cent. silver.

The hyponitrite had thus in these cases, as expected, suffered some oxidation, and had given us products nearly as low in silver as those analysed by Berthelot and Ogier—or, regarding as we do our preparations as having been dry, or nearly so, a still lower percentage than theirs.

It seemed to us most remarkable that a silver salt should contain 1.1—1.5 per cent. of water, as Berthelot and Ogier had found the hyponitrite to do, after drying *in vacuo* over sulphuric acid, and in order to determine to what extent water might be present in our own preparations, we tested two of them. No precautions against slight atmospheric oxidation were taken in preparing them. They were dried at the ordinary temperature in the Sprengel vacuum with sulphuric acid for about two days. The tube containing the dried salt having been sealed off from the sulphuric acid holder, was connected on one side with drying tubes through which carbon dioxide was passing, and the sealed point broken off. The other point having also been broken, the tube was on that side connected with a tube of heated copper turnings and a weighed calcium-chloride tube. The tube was then heated so as to decompose the hyponitrite, and the current of carbon dioxide continued for some time. An increase in weight in the calcium-chloride tube was found to have occurred.

VII. Hyponitrite yielding 0.0006 gram water was found to have contained 0.3041 gram silver. Assuming that the salt contained 76.5 per cent.—and a small error in this assumption is of no moment—we find a percentage of water amounting to 0.15.

VIII. With 0.6258 gram silver was found 0.0017 gram water, equal to 0.21 per cent.

These quantities of water are only the seventh of what Berthelot and Ogier got, but even so, their presence is abnormal. Blank experiments have made us certain of our results, but we believe this water may have come from some organic impurity, and not have been mere moisture. This is a matter we have yet to investigate. We have assumed that our other preparations contained only such small quantities as here found.

To avoid oxidation during washing, we now used subsidence and decantation instead of filtration, and transferred the salt suspended in

water to a drying tube to be connected with the Sprengel pump as in other experiments. It is necessary briefly to describe this tube. Tubing of about 2 cm. diameter was drawn out at the ends, and at an intermediate point much nearer one end than the other. In this way the tube formed two receptacles, one for the hyponitrite, and one, about 3 decim. long, for the sulphuric acid. The contracted part of the tube which separated them was bent into a rising curve, and the drawn-out ends of the tube were also bent into convenient form. The hyponitrite was introduced into the smaller receptacle by means of a slender funnel in this case, but in some other cases by means of a slender siphon. This end of the tube was next sealed off and sulphuric acid run into the other receptacle, which was then put in connection with the Sprengel pump. When the evaporation of the water—dry ice that is—was finished, the tube was sealed off from the pump, and after standing for the desired time, the two receptacles were separated also by sealing. Just before weighing the tube of hyponitrite, one end was broken off to admit air.

IX. Silver hyponitrite, 0.1302 gram, thus prepared, gave 76.59 per cent. of silver, and therefore no improvement in return for our precautions.

X. This experiment was like the last, but with the difference that after drying in the vacuum at the ordinary temperature, the receptacle holding the hyponitrite was heated to 60° C. for two hours before sealing off from the pump. Not a trace of gas was liberated, and the salt remained unaltered in appearance, besides being completely soluble in ammonia and dilute nitric acid. The quantity of hyponitrite taken was 0.5247 gram, and the percentage of silver found 77.06, which was a marked improvement upon previously obtained results.

Carbon dioxide has no sensible decomposing action upon silver hyponitrite, but, when in solution, dissolves it slightly, like acetic acid. In order therefore to exclude air during the purification of the hyponitrite, its dissolution in nitric acid, reprecipitation with sodium carbonate, and washing with de-aërated water, with dilute acetic acid, and again with water, were all carried on in a closed bottle fitted with tapped funnel, carbon-dioxide supply tube, and exit siphon-tube. When raised, the siphon-tube led off gas, and, when pushed down, either washings or hyponitrite suspended in water at pleasure. This tube was so narrow that the silver hyponitrite could be easily pressed up it with the water by the carbon-dioxide gas, in spite of its tendency to subside. By means of this siphon the salt, when ready, was transferred to the drying tube previously filled with carbon dioxide, and charged with sulphuric acid. The drying tube was then connected with the Sprengel pump.

XI. Hyponitrite, 0.2737 gram, gave 77.13 per cent. of silver.

XII. In an experiment the same as the last, but in which the effect of a final heating to 60° C. for nearly two hours was tried, hyponitrite, 0.2703 gram, gave 77.09 per cent. of silver. We were therefore disappointed in the effects of heating, and did not again resort to its use.

The numbers, 77.06, 77.13, and 77.09, were still a little more than 1 per cent. below the percentage for the formula AgNO , but nevertheless were about 1 per cent. higher than that required by Berthelot and Ogier's formula, and 2 per cent. above their actual numbers. Considering now that we might perhaps succeed in removing obstinately adhering nitrite or nitrate by repeated dissolutions and reprecipitations in the absence of air, we made two experiments in accordance with this notion. In the bottle, arranged as already described for working in an atmosphere of carbon dioxide, three dissolutions and reprecipitations with intervening washings were made. The sodium carbonate used for precipitating must be of special service in decomposing any silver nitrite and nitrate. In the first experiment we used acetic acid after each precipitation in order to dissolve out any silver carbonate that might have been formed. In the other experiment we omitted the use of the acetic acid after the final precipitation. We have sufficient reason for believing that no silver carbonate remained with the hyponitrite in this case, but will point out that supposing a trace did remain, it would have no effect upon the percentage of silver, for carbonic acid and hyponitrous acid have the same combining weight.

XIII. Hyponitrite, 0.2452 gram, gave 77.69 per cent. of silver.

XIV. Hyponitrite, 0.2977 gram, gave 77.53 per cent. of silver.

These are the highest percentages we have as yet got—0.8 to 0.6 per cent. of silver too low for the formula AgNO , but we fully expect to improve upon them. On comparing the analyses we have recorded in this paper with those published in the first communication on the subject by one of us, it will be seen that there is very little difference between their results.

Our experiments are incomplete, but we believe them sufficient to show beyond reasonable doubt that silver hyponitrite prepared in the usual way, is a salt of the composition AgNO , although mixed with products of its oxidation.

On the Preparation of Alkali Hyponitrite Solution.

Three distinct ways of preparing alkali hyponitrites have been published. The first, by one of us, is the reduction of alkali nitrite in solution by sodium or potassium amalgam; the second, by Menke,

is the reduction of fused nitrite by iron; and the third, by Zorn, is the reduction of dissolved alkali nitrite by ferrous hydroxide. In all three cases nitrate may be used to begin with in place of nitrite.

First Method.—In a paper of which we have only been able to see abstracts, Zorn expresses a preference for the use of ready-prepared nitrite for reduction by sodium.* With regard to his preference we may point out that the advantage of starting with nitrite is not so certain as it may seem to be. There must be taken into consideration the comparative purity of easily obtained nitrate and the usually great impurity of commercial nitrite, causing waste of much silver hyponitrite in the process of purification. Preparation of the nitrite in one's own laboratory removes this disadvantage, it is true, but still leaves the trouble to be taken. It must be further remembered that nitrite thus prepared in the ordinary way contains still a considerable quantity of nitrate, so that the saving of sodium for deoxidising is less by far than half. Unless, too, the lead process be used, heating the nitrate in a cast-iron or even wrought-iron pot imparts phosphate to the salt, and we know of no very easy and satisfactory way of purifying silver hyponitrite from phosphate.

The preparation of hyponitrite by electrolysing a solution of alkali nitrite with mercury as the negative electrode, has also been described by Zorn. This is in reality a modification of the sodium-amalgam process. Its success is very interesting, for in the absence of mercury, as Thorpe has shown, the electrolysis of solution of sodium nitrite yields hydrogen and sodium hydroxide at the negative pole, and no hyponitrite anywhere. When mercury is used, some of the sodium formed is preserved in the mercury almost from the first, and soon becomes comparatively stable in it through the accumulation of sodium hydroxide in the solution. After a time, and before the completion of the reduction of the nitrite, the mercury, if not too abundant, grows pasty and even semi-solid from the presence of much sodium. It is evident that it is this sodium which converts the nitrite to hyponitrite and some hydroxylamine, just as much here as in the ordinary amalgam process. We have not seen Zorn's paper, and it may be that he has himself given this explanation. For the

* From the abstract in *Watts's Dictionary*, Third Suppl., the reduction of nitrite to hyponitrite by Zorn might appear to be something new, which is not the case. One of us, in the original paper, mentions, in describing the production of hyponitrite from sodium and nitrate, that the metal first converts the nitrate into nitrite which is then easily obtainable, and that the nitrite is next reduced to hyponitrite by more sodium. Even the use of nitrite to begin with was too obvious from the first to have escaped his attention, although no mention of its trial—or, indeed, of any unessential particulars of the preparation of hyponitrite—occurs in this paper. All hyponitrite is the result of the reduction of nitrite when the sodium process is used, and doubtless also in other processes.

same reason we do not know the details of his mode of proceeding. We ourselves kept the positive electrode apart from the nitrite solution by enclosing it in a porous cell, and in this we put potassium hydroxide solution. Otherwise the sodium is formed by the decomposition of some of the nitrite—a very serious matter, because two atoms of sodium are necessary to deoxidise one molecule of sodium nitrite. As with the ordinary amalgam process, the yield of hyponitrite is far below the calculated quantity. We have spent much time upon this process, with the result that, situated as we are, we much prefer sodium to the galvanic battery to work with in making hyponitrite.

It is worthy of note that Zorn here prefers to make his sodium amalgam at the moment (and at the cost of his nitrite ?) instead of previously preparing it, while in his first process he chooses to prepare his nitrite first, instead of making it at the moment and at the cost of his sodium.

Second Method.—Menke heats potassium or sodium nitrate with iron-filings, and with or without sodium carbonate, for an hour after deflagration has taken place, preferring a charcoal fire as the source of heat. We have followed his instructions—which, we suggest, might with advantage have been fuller—but we have hitherto failed to get any hyponitrite. Zorn, too, states that he has tried Menke's process many times and in many ways, and has always entirely failed. He considers that Menke has mistaken phosphate for hyponitrite of silver. But we find given the determination not only of the silver but of the nitrogen in the salt, and a description of the sodium salt in crystals. Menke, besides, seems not to have been off his guard against mistaking phosphate for hyponitrite, although he tells nothing of the method he adopted for distinguishing and separating the hyponitrite from the phosphate which, with cast iron especially, he must have had present in quantity.

Third Method.—Zorn has described in his last published paper a third method of making hyponitrite by using ferrous hydroxide as the reducing agent. We have repeatedly tried this method, but have hitherto been disappointed in getting any success with it. We have not yet, however, given that rigorous examination to the process which alone would lead us to say that the process will not eventually succeed in our hands. Reduction proceeds readily enough, but we have not found any hyponitrite among the products. We intend to make further experiments.