Preparation of Hyponitrite from Nitrite through Oxyamidosulphonate.

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Through sulphonation followed by hydrolysis, an alkali nitrite is readily converted into the unstable oxyamidosulphonate, which, in a solution saturated with potassium hydroxide, gets all its hydrogen replaced by potassium and is at the same instant resolved into hyponitrite and sulphite—$2HONH.SO_3Na+4KOH=(KON)_2+2KSO_3Na+2OH_2$. This remarkable change was made known by us in 1889 (this Journal, **3**, 211), along with the fact that in it a rich source of hyponitrite had been lighted upon, since at least half the quantity of hyponitrite equivalent to the nitrite taken could be secured. But this productiveness, it was pointed out, depended upon our method of getting oximidosulphonate being employed, and the description of the method was not published till five years later, before when, consequently, the new source of hyponitrite could not be used advantageously by others. Even since then the method has escaped the notice of seven separate workers upon hyponitrites, Thum, W. Wislicenus, Paal and Kretschmer, Tanatar, D. H. Jackson, Piloty, and Hantzsch and Kaufmann, to be at last, however, taken up by Kirschner (*Z. anorg. Chem.*, 1898, **16**, 424). Indeed, it may be said to have been rediscovered by Piloty, who, in a paper upon 'an oxidation of hydroxylamine by benzenesulphonic chloride,' (*Berichte*, 1896, **29**, 1559), describes the resolution of benzenesulphonic hydroxylamide by potassium hydroxide into hyponitrite and benzenesulphinate, with a yield also of half the calculated quantity of the former salt.

As we have, each of us, very many times practised the oxyamidosulphonate method of getting hyponitrite and have not published the details of work which must be attended to in order to get high yields, it seems to us that we shall be doing a service by describing how to work the process.* After so much experience, we ourselves can count on getting a yield of sixty per cent. of the theoretical quantity (occasionally getting much more but without discovering how we had been so successful). The full quantity of silver hyponitrite would be just twice the weight of the sodium nitrite, while we get one-and-a-fifth times its weight. In what follows we assume that the convenient quantity of 2 decigram-molecules of sodium nitrite is taken, from which about 17 grams of silver hyponitrite may be obtained.

In order to limit the quantity of potassium hydroxide required, which is very large in any case, no more water than is necessary must be used. Except for the particular attention to be given to this point, the process begins exactly like that of making hydroxylamine sulphate from nitrite (This Journal, 1896, **9**, 291). In a tared, wide-mouthed, round-bottomed flask of 200-250cc. capacity, 14.4 grams of 96 per cent. sodium nitrite,** together with sodium carbonate containing 10.6 grams of anhydrous carbonate, are dissolved by heat in enough water to

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* Kirschner's method is an excellent form of our process, but I prefer that described in this paper.—E.D.

** But, preferably, 13.8 gr. pure sodium nitrite, this being now very easy to prepare (this vol. p. 15).

make the whole contents weigh 83.5 grams. (Some lead salt in the nitrite deposits, but goes into solution when the potassium hydroxide is added and gives no trouble). Sodium carbonate of any hydration may here be used but as, later on, more of this salt will be wanted and then should be approximately the monohydrate, it is convenient to use this form throughout. Such a carbonate, almost pure, is generally found in the 'dried' pure carbonate of commerce. Keeping the flask in active motion in an ice-and-brine bath, sulphur dioxide is passed in until a short time after the temporarily precipitated acid-carbonate has redissolved and when a bit of lacmoid paper in the solution becomes fully red. About $\frac{1}{10}$ cc. strong sulphuric acid is then dropped in. Thus carried out, always below 0°, the conversion of the nitrite into oximidosulphonate is perfect, while much above 3° some nitrilosulphonate would form and disturb everything. If such higher temperatures have been avoided, the nitrite and carbonate taken in close molecular proportions, and the sulphur dioxide not used in excess, the solution is ready to be hydrolysed ; but as the proportions of the salts may have been a little out and also sulphur dioxide be present, it is best to blow a strong current of air through the solution before its temperature has risen, so as to expel any sulphur dioxide or nitric oxide that may be present.

After this treatment, the solution is brought to about 30°, in order to start hydrolysis, then set aside for a day, in a warm place, with the flask corked. Complete hydrolysis to oxyamidosulphonate without further hydrolysis to hydroxylamine is thus secured,* and, consequently, just the calculated

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* This success in avoiding production of hydroxylamine has been proved by shaking the solution, after it has been made alkaline, with sodium amalgam which readily converts

quantity of sodium carbonate (10.8 grams anhydrous) is found to be required, including that for the three or four drops of sulphuric acid added. The approximately monohydrated carbonate, in fine powder, is quickly shaken thoroughly with the solution, so as to hinder its caking, and the last portions of it then dissolved up by warming the flask. The solution of oxyamidosulphonate and sulphate, thus prepared, contains almost exactly only half its weight of water, is therefore supersaturated, and is the strongest solution practically obtainable; it will be found to approach closely 113 grams in weight, so smoothly do the reactions proceed. To make a weaker solution and then concentrate it by evaporation is easy enough, but the adjustment is troublesome and the formation of hard cakes of sodium sulphate, which interferes with the proper working of the next stage of the operation, is difficult to avoid.

The flask is well drained of its contents into a basin, preferably a hemispherical nickel basin or, lacking that, a stout porcelain one, of capacity not much less than 500cc. Potassium hydroxide, free from chloride, assayed for real alkali and for water, and having not less than $\frac{2}{3}$ and not more than 1 mol. water to 1 of the hydroxide, is now needed; for if it were anhydrous it would cause much heating and consequent decomposition of the salts. Generally, the potassium hydroxide purified by alcohol and the more translucent varieties of stick potash contain about the right proportion of water and then

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hydroxylamine to ammonia and is inactive upon oxyamidosulphonate. Testing in this way, no odour of ammonia has been recognisable and moist red litmus paper held in the bottle has been barely affected. Kirschner, using potassium oximidosulphonate, had to heat to boiling to effect hydrolysis, which is difficult then to complete without some of the oxyamidosulphonate passing on into hydroxylamine. When the hydrolysis is underdone, there will be nitrite regenerated later on by the alkali; and when it is overdone there will also be nitrite formed during the oxidation of the hydroxylamine by the silver (or mercury) oxide.

dissolve in water without much rise of temperature. From 130 to 165 grams of it, according to its degree of hydration, are quickly crushed in a warm mortar and thrown into the solution in the basin and incorporated with it by means of a pestle. There is marked heating only just at first, which is better met by keeping the basin in water or resting on snow or pounded ice for a very short time. On stirring-in the potassium hydroxide the solution sets to a stiff paste, if kept cold, quickly becoming thin again by further stirring, but full of opaque white precipitate of sulphate. If the basin has been cooled, hardly any gas escapes at first, but gentle effervescence and much frothing occur before long in any case. When the potassium hydroxide has been all ground up and dissolved, the basin is placed under close cover from atmospheric moisture and carbonic acid, and left so for 30 hours in a warm place (Kept for more than 50 hours, the quantity of hyponitrite sensibly but slowly diminishes). As much even as one-fourth of the oxyamidosulphonate may sometimes in cold weather still be present and can be partly destroyed by keeping the basin at 55–60° for half an hour, though not with noticeable increase of the quantity of preserved hyponitrite. This heating, with the risk attendant on it of destructive over-heating, is better omitted, on the whole. Besides undecomposed oxyamidosulphonate, the contents of the basin now consist of precipitated sulphate and sulphite, and solution of potassium hydroxide in slightly less than its weight of water (almost exactly, $KOH:3H_2O$), together with the potassium hyponitrite. It is, apparently, only to secure this concentration of the potassium hydroxide, a practically saturated solution, that hardly less than 10 mols. of it to one oxyamidosulphonate have to be used. More of it may be added without effect, good or bad, unless the solution of the salts is weaker than it is here advised to be, for in that case additional potassium hydroxide must be taken to bring its concentration to the right point.

Treatment with a silver salt is the only way of separating the hyponitrite from the other salts, and for this purpose the presence of the alkali is essential, together with large dilution when precipitating. The best way is to use the silver solution exceedingly dilute, because this checks the precipitation of silver oxide and sulphite until some time after hyponitrite has been all separated. Now, the need for large dilution and the advantage of still larger dilution remove the only objection that can be raised to the use of silver sulphate instead of silver nitrate; and since it is generally important to feel assured that no trace of nitrate or nitrite can have been added to the hyponitrite, the sulphate should have the preference, although the nitrate can almost certainly be used with as good results. A cold saturated solution contains only 5 or 6 grams of the sulphate to the litre, and is most easily prepared by boiling excess of the salt with water and pouring the solution into an equal volume of cold water.

Whichever salt is used, the contents of the basin having been washed into a very capacious precipitating vessel, the highly dilute silver solution is poured in until it ceases to produce any more black precipitate. When this is at all abundant, as it sometimes is in winter weather, an hour's interval is given for subsidence of most of it, the still dark solution decanted, and the precipitate washed by decantation before rejection. With or without this interruption, the addition of the silver solution is continued until the bright yellow hyponitrite suddenly appears, and so long after as the joint precipitation of brown oxide is easily checked by stirring. When the point is reached where the oxide only redissolves slowly and no longer gives place to a yellow one of hyponitrite, no more silver solution must be added. To add much more would be to cause permanent precipitation of silver oxide, which, if at all large in amount, is apt to be accompanied by silver sulphite. The quantity of silver sulphate needed may be as much as 40 grams, which means 7 or 8 litres of solution; of silver nitrate about 44 grams will be wanted, dissolved in 4 litres, or more, of water.

Half an hour after precipitation, the solution is to be poured off even though still a little turbid, and the precipitate washed by decantation; for very slowly deposition of a mirror of metallic silver from the sulphite in solution begins and goes on for days. In order to separate the hyponitrite from the metallic silver and its oxide, and perhaps chloride, it has to be dissolved in dilute acid and reprecipitated. If every trace of nitrite is to be kept out of the hyponitrite, nitric acid can hardly be used, because it always contains, according to my testing, a very minute quantity of nitrous acid. Sulphuric acid is therefore the acid to take. Since the hyponitrite must be kept in solution the shortest time possible for filtration, the use suggests itself of acid not very dilute in order to reduce the volume of liquid to be filtered. But high dilution is better, because the stability of hyponitrite falls off rapidly with increasing concentration, and, besides this, the use of sulphuric acid not dilute enough causes separation of silver sulphate. A one per cent. solution of the acid is suitable, after it has been well cooled in ice, some five litres of it being probably required.

The precipitate should be treated with the acid in portions at a time, not all together; and as far as possible undissolved precipitate should be kept off the filter till the last. For so long a filtration a Lunge's filter tube extension of the funnel is more suitable than the filter pump. The filtrate is to fall direct into excess of sodium carbonate solution. Working with these precautions, the silver hyponitrite can be dissolved and reprecipitated, even in hot weather, with hardly appreciable loss.

Having replaced the mother-liquor by water, dilute sulphuric acid is cautiously added until, after good stirring up of the precipitate, the solution is no longer alkaline and some of it filtered is found to contain dissolved a trace of the silver hyponitrite, this being best ascertained by adding one or two drops of sodium carbonate solution to about 100 cc. of it, which should cause a permanent yellow, very slight opalescence.

The precipitate, thoroughly washed by decantation and dried on a filter at the common temperature in a desiccator in the dark, and then at 100°, will give 78 per cent. silver (calc., 78.26). But in order to preserve the bright colour of the salt and its entire freedom from nitrite, all work upon it should be done with very little exposure to bright daylight. Its weight should be not less than 17 grams.

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